

Applied Infrared Spectroscopy

Edited by

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Foreword

From a little-known and virtually unused method two and a half decades ago, infrared spectroscopy has now reached a status of general acceptance and utility unequaled among the analytical methods of organic chemistry. Moreover, through continued development of better instrumentation and new techniques, its usefulness appears to be expanding as rapidly today as ever.

It has been an interesting observation that as infrared spectroscopy first made its way into each new field, it often evoked the enthusiastic accolade of seeming *especially created* for that particular field. Long ago a friend of mine made the comment that "infrared may indeed be useful for the carbon compounds but it was *invented* for the silicon-organics." Similar homage paid by several authors in this book can be quoted:

"The infrared method was almost custom-built for the essential oil industry."

"... more widely used in solving polymer problems than any other type of problem to which the infrared technique is applicable."

"... uses which are more or less unique to the pharmaceutical field ..."

"Progress on the question of the structure of coal continues, and infrared spectroscopy is one of the chief contributors to this progress."

"No single tool has had a more dramatic impact on organic chemistry than infrared measurements."

Granted a glowing record of past accomplishments, infrared spectroscopy promises a still more brilliant future. A tool of this great power invites a complete reorientation, a rethinking of the manner of its use by the chemist in the laboratory and by the engineer in the plant. The design of chemical experimentation is evolving to realize optimum advantage of the fast, specific method of analysis, and the chemical plant is beginning to rely heavily upon continuous analytical readout for process control.

Perhaps the greatest of all its promises is in the realm of fundamental chemistry since the infrared spectrum reveals information not only of analysis and structure but of the distribution of electrons throughout the molecule, which is the origin and the very essence of its chemical nature.

NORMAN WRIGHT

The Dow Chemical Company

Preface

Our purpose is to present a volume on the practical applications of the techniques of infrared spectroscopy so that a scientist may be encouraged to apply them to the solution of his own problems.

The applications covered concern principally empirical infrared absorption spectroscopy applied to problems arising in the fields of chemistry, physics, and biology taken in their broadest sense. The identification of unknown materials, the determination of chemical structures, the following of the course of a chemical reaction, the distinguishing of spatial isomers excluding optical enantiomorphs, the making of a choice between potential chemical structures, the assay of chemical purity, the development of quantitative analytical methods, and the guidance given to research, development, and quality control - these are some of the applications treated.

The contributors are leaders in at least one specialized sub-field of infrared. They have attempted to share their know-how, gained over years of experience, to help the reader in his attack on a problem amenable to infrared techniques. Their aim is to ease the introduction of the neophyte into infrared and their special region of it, as well as to indicate the pathways for the experienced spectroscopist who up until now has had no occasion to apply infrared to "their specialty."

Both the principles underlying infrared laboratory instrumentation and the application of these to plant stream analyzers are thoroughly discussed. The normal as well as the specialized techniques developed to obtain the ultimate in spectroscopic information from very small samples, unusual samples, and samples at high pressures are described. The types of samples for which ATR is the indicated procedure are detailed. The ever widening applications of infrared to inorganics are presented. What infrared can accomplish in the spheres of polymers, pharmaceuticals, essential oils and cosmetics, and in coal structure research, is discussed. How infrared is applied to problems arising in the government regulatory agencies is thoroughly covered. The use of computers in spectroscopy is detailed. How infrared is used at the chemist's bench and in the industrial infrared

laboratory is explained. Note is made of recent advances in infrared which show future promise for enlarging the scope of problems which can be successfully attacked.

The background material on which empirical infrared spectroscopy is based has been treated only briefly in this volume, since more intensive and detailed treatments are already available. References to the latter are given at appropriate places.

The editor has observed a lack of a brief general procedure for the qualitative interpretation of an infrared spectrum. This he has supplied to fill the void experienced by many beginners when they first enter into the "wonders" of what empirical infrared spectroscopy can contribute to the solution of scientific problems. This procedure is based on a lecture first given at Fisk University.

This volume purposely neglects a few important subdivisions of infrared. It is not intended to cover every aspect of this vital technique but only certain selected applications of widespread interest. The reader must also expect differences in style and approach and some overlapping of content. This is willful, since the editor believes a specialist should present his own case and let the reader be the jury.

Vincent J. Coates and Abraham Savitzky conceived the idea for this book and had selected several of the contributors when increased responsibilities at the Perkin-Elmer Corporation prevented them from continuing.

The willingness of the contributors to take precious time from their active careers to present certain of their findings for this volume is greatly appreciated. Their cooperation and understanding eased the task of editing.

My thanks to Dr. Norman Wright for reading the entire manuscript and making valuable suggestions which improved the book.

The personnel of Reinhold Publishing Corporation were most helpful in smoothing the way.

The editor is greatly indebted to his wife and secretary (the same) for her assistance.

DAVID NELSON KENDALL

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CHAPTER

Infrared Radiation: Description and Simple Theory of Absorption by Molecules

David N. Kendall

INTRODUCTION

Infrared spectroscopy is the most useful tool available to the scientist for the solution of problems having to do with molecular structure, molecular behavior, and the identification of unknown organic chemical substances and mixtures. Although this method is decades old, its application to the solution of inorganic chemical problems is still in its infancy.

The infrared spectrum of a material which absorbs this radiation constitutes a "fingerprint" of the material - an actual analysis of the motions the molecule is undergoing at the temperature at which the sample is scanned. By contrast to the single physical value represented, e.g., by a melting point or a boiling point, an infrared spectrum of a molecule can offer thirty to fifty physical data with which to work, all capable of yielding information to the informed.

Given a specific molecular structure, theoreticians can calculate the frequencies at which infrared radiation will be absorbed by this molecule, provided the spatial arrangement of the atoms and the strengths of all the forces among the atoms are known or can be determined. The complicated nature of such calculations, despite modern computers, is overwhelming for most molecules of industrial interest, since the number of atoms in the molecule and their arrangement in space make the theoreticians's calculations extremely difficult, tedious, and often inaccurate for lack of enough known data.

For a few molecules containing a small number of atoms, or for a few "large" molecules of high geometrical symmetry, the mathematical treat-

ments have been excellent. However, since most molecules of commercial interest are quite complex, another method is necessary to correlate observed absorption peaks and their transmittances with the structure of a given molecule. Such an approach is the empirical method, which has already yielded solutions to a host of scientific problems.

THE EMPIRICAL APPROACH

In brief, the empirical or "experience" method involves comparing the spectra of the largest obtainable number of different molecules having a common atomic group, including molecules of as great dissimilarity as possible, provided that they contain the common atomic grouping. It is often possible to find one or two absorption bands whose frequencies remain reasonably constant throughout the array of molecules. Thereafter, the presence of an absorption band in the spectrum of an unknown material at this frequency or frequencies forms the basis on a 95% chance level that this specific atomic grouping is present in the unknown material. The vast majority of useful information obtained from infrared spectra is derived by the empirical method.

As with any other scientific technique, the results obtained from infrared absorption spectroscopy investigations are no better than the ingenuity and the knowledge of the investigator. The able and skilled practitioner can solve problems which appear impossible to some infrared spectroscopists. The eye, brain, and hands of the investigator are much more important than the instrument, or whether energy is plotted U.S. or English style.*

Before delving further into the empirical infrared procedure and its possibilities, infrared radiation and its interaction with matter will be briefly considered.

THE NATURE OF INFRARED RADIATION

Infrared radiation is electromagnetic in origin, just as are x-ray, ultra-violet, and visible radiation. All electromagnetic radiations are governed by the same mathematical laws. Owing to the variations in their frequencies (wavelengths) they exhibit different properties, and different means are used to emit them, disperse them, and detect them.

Electromagnetic radiation is both particle-like and wave-like in nature. The energy (E) of any such radiation can be expressed by the equation

$$E = h\nu \quad (1-1)$$

*The U.S. custom is to plot % T on the ordinate vs wavelength (or frequency), while the English convention is to plot % absorption vs wavelength (or frequency).

where h is Planck's proportionality constant and ν is the frequency of the radiation. Equation (1-1) is Planck's law, which forms the basis of the quantum theory. One of the results of quantum theory is that radiant energy is "quantized," that is, it comes in discrete packets rather than being a continuum.

Subdivisions of the Infrared Region

The infrared spectral region covers the electromagnetic radiation range from about 0.75μ to 1 mm. Infrared rays are invisible to the human eye, so the lower limit of the infrared region is taken as about 0.75μ where normal human vision ends. The upper limit of the infrared region is usually considered to end somewhere between infrared and microwaves at about 1 mm. Since microwaves have quite different properties and are produced, detected, and used in quite different ways from the usual infrared radiation, it is useful to consider that the infrared region ends on the long-wavelength side, where microwave techniques begin.

The infrared region is subdivided into the near infrared, the medium or fundamental infrared, and the far infrared. The reasons for this subdivision are that there are variations in the instrumentation employed in each subdivision, and also differences in the kind of information obtained from each region.

Near Infrared. The near infrared extends from about 0.75 to 3μ and it is so delineated because photographic emulsions and photoelectric cells can be used over this wavelength region. Overtones of hydrogen stretching (str) vibrations are observed in the near infrared. They have particular usefulness in certain qualitative and quantitative analyses whenever OH, NH, and CH chemical groupings are concerned.²³

Fundamental Infrared. The fundamental infrared encompasses the region from 2 to 25μ and is often called the "prism infrared," because the first commercial instruments used prisms to disperse the radiation.

This volume concerns itself almost exclusively with the fundamental infrared, wherein the majority of molecular vibrations of chemical significance occur, and which therefore is the most widely useful region of the infrared electromagnetic spectrum.

The first and still most useful prism is NaCl, applicable from 2.0 to 15.0μ . It was followed by KBr, useful from 15 to 25μ . In recent decades KRS-5 (thallium bromo-iodide), CsBr, and CsI have extended the range of prisms to 50μ .

With the commercial introduction of gratings as dispersing means (about 1959), their use has come to the fore and they will in time largely replace prisms. Currently, however, a vast amount of "spade work" needs doing to uncover and correlate with molecular structure the "new" absorp-

tion bands provided in infrared absorption spectra through the use of gratings. It will be several decades at least before prism infrared instruments are obsolete.

In the fundamental infrared the most commonly used sources of radiation are the Nernst Glower, a mixture of rare earth oxides; the Globar, silicon carbide, and heated ceramics (see Chapter 3).

Far Infrared. The far infrared extends from about 25 to 1000μ (400 to 10 cm^{-1}). Rotational transitions and lattice modes of crystals occur in the far infrared. A filter grating system (see Chapter 3) can be used out to 300μ at present, and the Golay pneumatic detector is the most widely used radiation detector. The high-pressure mercury arc with quartz tube is the usual radiation source.

Units Used in Infrared

The velocity of propagation of wave motion is expressed by the well-known relation

$$\bar{\nu}\lambda = c \quad (1-2)$$

where λ , the wavelength in cm, and $\bar{\nu}$, the frequency in cps (cycles per second) have as their product $c = 3 \times 10^{10}$ cm/sec, the velocity of light.

In the infrared, for numerical convenience, λ is usually expressed in microns, μ ($1\mu = 10^{-3}\text{ mm} = 10^{-4}\text{ cm}$), and $\bar{\nu}$ is expressed in terms of the number of waves/cm or wave number. The number of waves/cm, ν , is

$$\nu = \frac{\bar{\nu}}{c} \quad (1-3)$$

Since the dimensions of $\bar{\nu}$ are cps and of c are cm/sec, the dimensions of ν are cm^{-1} (reciprocal centimeters).

From Equation (1-3), $\bar{\nu} = c\nu$, so substituting in Equation (1-2), $\lambda \cdot c\nu = c$ or $\lambda\nu = 1$. Expressing wavelength in microns rather than centimeters, then

$$\lambda\nu = 10^4 \quad (1-4)$$

In summary, the infrared spectroscopist commonly uses μ (micron) to express wavelength, and cm^{-1} (wave number) to express frequency. Prism spectrophotometers are usually linear in wavelength, grating instruments linear in frequency. The spectroscopist should learn to think in terms of either μ or cm^{-1} . Since frequency and wavelength are not independent of each other, neither can be considered more fundamental. Frequency, however, is often the unit used in theoretical work and the unit of choice in Raman spectroscopy, which complements infrared in molecular structure studies.

In this volume, sometimes frequency will be used and sometimes wavelength, and values will be expressed in both units. As a practical matter,

almost all infrared spectra recorded on preprinted charts show both μ and cm^{-1} .

The Spectrum and Beer's Law

An infrared spectrum is simply a plot, obtained manually or automatically, of a function of radiant power (energy) along the ordinate vs frequency or wavelength as abscissa. Commonly one plots transmittance ($\%T$) or absorbance (A) of radiation vs cm^{-1} or μ . The major interest is in those frequencies at which a material absorbs radiation and the amount absorbed. These absorption "peaks" or minima give rise to the uniqueness of the absorption spectra of different materials.

Radiant power, P , is the time rate at which energy is transported in a beam of radiant energy. If P_0 represents the radiant power incident on a sample and P the radiant power transmitted by that sample, then, by the Beer-Lambert-Bouguer Law,⁴ (abbreviated hereafter as simply Beer's Law)

$$P = P_0 e^{-abc} \quad (1-5)$$

where

a = the absorptivity, the inherent absorbing power, in units of one's choosing, of the radiation at a specific frequency, ν

b = the path length of the sample in cm

c = the concentration of the sample in g/l (for solution work, e.g.).

Then

$$\frac{P}{P_0} = e^{-abc}$$

Now

$\frac{P}{P_0}$ = the transmittance, T , the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Changed to per cent, it is conveniently expressed as $\%T$ transmittance ($\%T$).

Thus

$$T = e^{-abc}$$

and

$$\log T = \log e^{-abc} = -abc$$

$$\log_{10} \frac{1}{T} = abc$$

Now $\log_{10} \frac{1}{T}$ or $-\log T$ is defined as absorbance, A , the \log_{10} of the reciprocal of the transmittance.

Thus

$$A = \log_{10} \frac{1}{T} = abc \quad (1-6)$$

The role which Equation (1-6) plays in quantitative analysis is described in Chapter 2.

Illustrated below is a typical infrared spectrum scanned over the 2.5 to 15 μ range.

The Origin of Infrared Absorption Spectra

In Figure 1-1, it is the absorption peaks or minima that are of the greatest interest. Why and how do they arise and what is their significance?

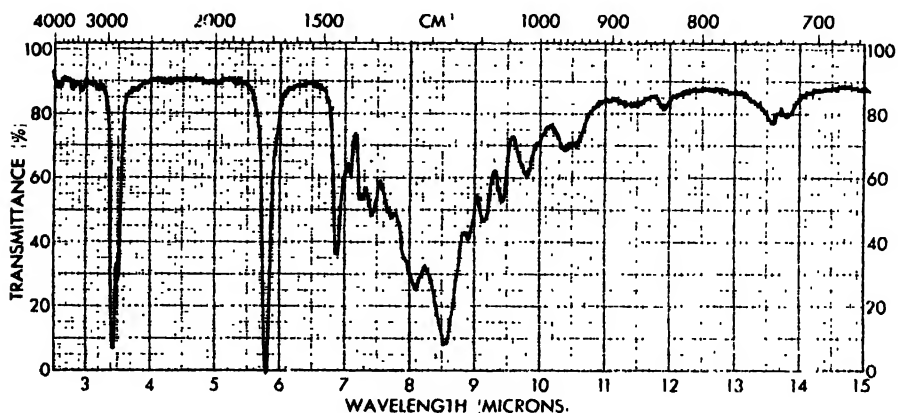


FIGURE 1-1. Infrared spectrum of dibutyl sebacate.

The frequencies of the oscillations which atoms of any molecule not at absolute zero temperature undergo (10^{13} to 10^{14} cps) fortunately are of the same order of magnitude as those of infrared radiations. One might predict that some relationship exists between the motions of atoms within molecules and their effects on infrared radiation of the same frequencies incident upon them.

Those molecular vibrations or motions, in general, that are accompanied by a change of dipole moment during the vibrations, absorb by resonance all or a portion of the radiation incident upon them, provided the frequencies of the radiation coincide exactly with the frequencies of the molecular motions.

It is not necessary that a molecule have a permanent dipole moment to absorb infrared radiation. CCl_4 with zero dipole, e.g., absorbs infrared because there are vibrations which the C-Cl groupings undergo, when they are not in phase, during which a change in dipole moment occurs.

As a consequence of the dipole moment change criterion, one does not expect infrared absorption from diatomic molecules comprised of identical atoms, such as N_2 , O_2 , Cl_2 , etc., since no change in dipole moment occurs

INFRARED RADIATION

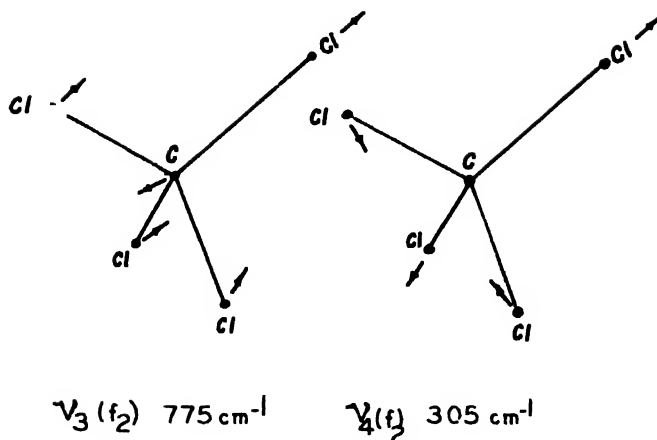


FIGURE 1-2. Infrared-active fundamental vibrations of CCl_4 .

during their vibrations. Nor are monatomic molecules or ions expected to absorb infrared. All the so-called inert gases* thus show no ordinary infrared absorption.

Diatomic molecules, however, in which the two atoms are not of the same kind, will show infrared absorption, because dipole moment changes occur during their vibrations. Thus, HCl , CO , NO , etc., show infrared absorption.

In general, covalent bonding between unlike atoms gives rise to infrared absorption, whereas ionic bonding does not. NaCl , KBr , and LiF , e.g., are excellent "windows" for infrared radiation and are used as prisms for dispersing such radiation and as plates to hold samples in the infrared spectrophotometer.

Binding between atoms which are part covalent and part ionic, as for both very many organic and many inorganic materials, will show absorption because of that portion of their bonding that is covalent in nature. Generally, all organic chemicals (substances) absorb infrared radiation. While diatomic inorganic substances, where the chemical bonding is almost exclusively ionic in nature, show no infrared absorption other than their relatively massive lattice vibrations, all inorganics containing polyatomic cations or anions or both yield useful infrared absorption. This is true because covalent bonding is involved in the polyatomic cations or anions. While K_2SO_4 can be distinguished from Na_2SO_4 only when both substances are pure and not together as in a mixture, the varying effects of cation and anion size, charge, and radius permit the identification of many sulfates

*The "inert" gases are not as unreactive as formerly believed. Compounds such as XeF_4 , XeO_3 , and KrF_2 , e.g., have been reported in the literature in the last few years.

even when present in mixtures. An additional help is the fact that polymorphic forms of both inorganics as well as organics can be distinguished by their infrared spectra. While LeComte,²⁸ Hunt, Wisherd, and Bonham,²⁰ Miller and Wilkins,³¹ Kendall²⁵ and others have shown how useful application of infrared techniques can be to the solutions of inorganic chemical problems, vastly greater exploitation of inorganics by infrared awaits enterprising investigators.

Intensities

The question now arises, to what extent do molecules or atomic groupings therein absorb infrared radiations. Equation (1-6) tells us the absorbance, A , is a linear function of the product abc . Now " a " is the absorptivity (or absorption coefficient) of any given material at a given frequency, ν . Since " b ," path length, and " c ," concentration, can be kept constant when comparing intensities of absorption bands, the significant question is, is " a " a fundamental property of a given molecular motion? While fairly insensitive to pressure and usually practically independent of temperature, slight variations in its value occur among the solid, liquid, and vapor phases caused by the varying extent to which the internal vibrations of one molecule are affected by those of its nearest neighbors. Consider, then, that intensities are being compared in the same phase, at the same concentration and path length: is " a " now an inherent fundamental property? It is when its value is derived from a spectrophotometer whose spectral slit width approaches zero. All commercially available spectrophotometers, however, have finite spectral slit widths, since such instruments are energy-limited because of the sources of infrared energy which must be used (see Chapter 3). Instrument manufacturers have not been able to duplicate exactly the spectral slit widths of infrared spectrometers, even of the same model and make. The value of " a " is also affected by the varying amounts of scattered light* which infrared instruments show at varying wavelengths. For the above reasons, absorptivity is not an unvarying, absolute, specific value for any given vibration. Infrared spectra cannot successfully be plotted as absorptivity vs frequency (wavelength), but for the foreseeable future will be plotted as % T (or A) vs frequency. This means that quantitative analytical data cannot be readily transferred from one spectrophotometer to another.

*Scattered light, known also as "stray radiation" and "false energy" arises principally from imperfections in optical surfaces. These allow small quantities of light of wavelength different from that for which the instrument is set to pass to reach the detector, thus becoming part of the amplified signal. As a result, the transmittance of an absorption band will be higher than its true value.

Scattered light is most serious at longer wavelengths. Source emission is relatively low at long wavelengths, compared to the 2 to 3 μ region. Hence, scattered light from the short-wavelength region, where source emission is high, can represent a substantial portion of the detector signal.

Absorptivity has very little theoretical significance when inherent absorption intensity of any given molecular vibration is considered, because it makes no distinction between narrow and wide bands. A wide absorption band equal in peak height to a narrow band must result from a greater absorption of infrared radiation, other factors being equal.

The total absorption of energy by a molecular vibration is given by the integrated intensity over the resulting absorption band. Theoretically the integrated intensity, I_f , is

$$I_f = \int_{\text{band}} a_{\omega} d\omega \quad (1-7)$$

where a_{ω} is the theoretical absorptivity value obtainable only when spectral slit width approaches zero, and the subscript ω shows it varies with frequency. Because all useful infrared spectrometers have finite spectral slit widths, Equation (1-7) becomes

$$I_f = \int_{\text{band}} a_{\omega} d\omega > B = \frac{1}{hc} \int_{\text{band}} \log \frac{1}{T_{\omega}} d\omega \quad (1-8)$$

Without going into detail, it can be shown that $I_f \cong B$, as the ratio of spectrometer spectral slit width* to band half-width† becomes small. This condition prevails only with spectrometers having resolving power of about 1 cm^{-1} or better. Grating instruments providing such resolution have recently become available. Unfortunately, integrated intensities are difficult to measure with accuracy and reproducibility, and certain rather arbitrary assumptions are necessary to arrive at values for I_f . Different investigators have come up with widely differing values for the I_f of the same molecular vibration of the same molecule. The theoretical and experimental basis for I_f 's is not yet on firm enough ground that it may be advantageously used by practicing spectroscopists.

In assessing relative intensities to be expected from vibrational modes of various functional chemical groups, the spectroscopist is usually most interested in how absorptivity, expressed through absorbance measurements, varies. In general, the greater the change in the dipole moment during any given molecular vibration, the greater the absorptivity. Thus, the C—F bond and the Si—O bond each has high "a." For saturated aliphatic hydrocarbons the C—H and the C—C bonds, particularly the latter, do not give rise to large dipole moment changes during vibrations. Therefore, one does not expect high intensity of infrared absorption for these groupings and this type of compound. Nonpolar compounds usually show low absorptivity, while polar compounds have large values of "a."

*The spectral slit width is, by definition, one half the width of the frequency range passed by the exit slit of a spectrometer.

†Band half-width is $\frac{1}{2}$ the width of an absorption band in cm^{-1} measured at the point of half the value of maximum absorbance.

SIMPLE THEORY OF INFRARED ABSORPTION BY MOLECULES

To understand empirical, i.e., experience, infrared spectroscopy, one needs briefly to examine the simplified theory of the absorption of infrared radiation by molecules. It will then become evident why one must resort to empirical spectroscopy to solve molecular structure problems concerning any but the smallest molecules.

Energy Levels in Molecules

The energy of a molecule, E_{mol} , is the sum of its translational, rotational, vibrational, and electronic energies:

$$E_{\text{mol}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} \quad (1-9)$$

Since E_{trans} has no significant effect on molecular spectra, it will be disregarded.

E_{rot} is entirely kinetic and depends on the geometrical form of a molecule and therefore on the moments of inertia of the molecule. For certain geometrical molecular forms, general mathematical expressions can be written for E_{rot} , but for most polyatomic molecules, whose three moments of inertia have three different values, no general expression can be written. Rotational energy is of consequence primarily for molecules in the vapor state which can rotate freely. For liquids and solids, molecular rotation is normally hindered or prevented completely by intermolecular forces, and molecular rotation absorption bands are not normally observed. Thus, rotational spectral studies are carried out almost exclusively on those molecules existing in, or which can be obtained in, the vapor state.

E_{el} is concerned with the three kinds of electrons in molecules: those which belong exclusively to a single atom, those which are shared by two adjacent atoms, and those shared by more than two atoms. The first-mentioned kind, inner shell electrons, contribute negligibly to E_{mol} and may be disregarded.

The second kind and third kind of electrons above are the ones involved in transitions between rotational and vibrational electronic energy levels when irradiated by ultraviolet or visible radiation. Since infrared radiation is less powerful in terms of energy, it does not normally excite such transitions. Hence, in studying the infrared region from 2 to 25 μ , one can consider E_{vib} reasonably separately from the other types of energy possessed by a molecule. Thus Equation (1-9) becomes:

$$E_{\text{mol}} \approx E_{\text{vib}} \quad (1-10)$$

Vibrational Energy Levels

In three dimensional space, a molecule of N atoms has $3N$ degrees of freedom, i.e., kinds of motion. Three are ordinary translation and three

are rotations about the three axes of inertia (two for a linear molecule since rotation about one axis is zero). There remain $3N - 6$ vibrational motions ($3N - 5$ for linear molecules). Each such vibrational motion has associated with it a vibrational frequency. Since these frequencies are of the same order of magnitude as the frequencies of infrared radiations, it is vibrational motions and frequencies with which the practicing infrared spectroscopist is primarily concerned.

When the frequency of incident infrared radiation is the same as the frequency of vibration of a grouping of atoms in a molecule and there is a change in dipole moment during that vibration, all or part of the incident infrared radiation will be absorbed by resonance.

As long as the vibrations are moderate, they are essentially harmonic. While the total vibrational pattern of a molecule is often quite complicated, any harmonic vibration is the superposition of two or more simple vibrations designated *normal* vibrations of the molecule. As seen above, there are $3N - 6$ normal vibrations and hence the $3N - 6$ frequencies associated with them are called *fundamental frequencies* of the molecule. These frequencies can be all different or there can be several pairs or triples of vibrations with the same frequency.

The vibrational energy levels of a molecule can be represented in a simple way as long as the vibrations are harmonic (i.e., obey Hooke's law). Each harmonic vibration contributes a set of energy levels to the total pattern, which is independent of the energy levels of the other vibrations. The energies of one vibration, W_{vib} , having frequency ν_1 , and the vibrational quantum number v_1 , are related in the manner:

$$W_{\text{vib}} = (v_1 + \frac{1}{2})h\nu_1 \quad (1-11)$$

where v_1 is 0, 1, 2, 3, . . . Each vibration has a separate quantum number, v , and the total vibrational energy pattern for the molecule results from summing up Equation (1-11) for all the $3N - 6$ vibrations:

$$W_{\text{vib}} = \sum_{i=1}^{3N-6} (v_i + \frac{1}{2})h\nu_i \quad (1-12)$$

where v_i is the vibrational quantum number of the i th frequency and ν_i is the frequency of the i th vibration.

It will be observed from Equation (1-11) that the energy levels of a single frequency are equally spaced with a spacing of $h\nu$, and that the lowest energy level, when $v = 0$, has an energy of $\frac{1}{2} h\nu$, and not zero. So even at absolute zero temperature the vibrator has energy, called the zero-point energy.

In actual fact, the purely harmonic conditions assumed above do not prevail for real molecules, because forces between atoms cannot be de-

scribed accurately by simple force constants but vary with interatomic separation in more complicated ways. Thus nonharmonic effects, or *anharmonicity*, is always present. This means that higher energy vibrational levels in particular will be crowded together somewhat, because the equal spacing concept of Equation (1-11) breaks down.

The effects of anharmonicity are in most cases extremely difficult to calculate mathematically for lack of essential theory and essential experimental data. Given a specific molecular structure, theoretical calculations to delineate the frequencies and intensities of its infrared absorption spectrum are not feasible for molecules containing more than three or four atoms.

The practical spectroscopist, in dealing with the vast majority of molecules of concern to commerce, industry, and the health sciences, must rely on experience—observation and correlation with molecular structure of the absorption spectra of thousands of molecules. This is empirical infrared spectroscopy.

Since shortly before the turn of the last century, scientists interested in this whole area have done just what is described above—observed and correlated with molecular structure the infrared absorption spectra of many thousands of molecules.^{1,2,6,22} Summarizing these investigations, it has been observed that many of the vibrational frequencies of a molecule are predominantly those of very small groups of atoms within the molecule, and these frequencies are characteristic of these groups of atoms no matter in what molecules they occur. This empirical observation, first formulated after the infrared spectra of only a relatively few molecules had been observed, is the basis for qualitative analysis of molecules and for the elucidation of molecular structure. These frequencies are called *group frequencies*.

Not all vibrational frequencies, however, are group frequencies. Each molecule undergoes vibrations which are characteristic of the molecule as a whole and are strongly dependent on the geometrical arrangement in space and the kind and masses of the molecule's constituent atoms. Such frequencies allow the infrared absorption spectrum of a molecule to serve as a "fingerprint"—to enable practically any molecule which absorbs infrared to be distinguishable from any other molecule which absorbs such radiation.

In addition to the *group frequencies* and *fingerprint or characteristic frequencies*, a spectrum of a substance shows *overtone and combination absorptions*, which arise from multiples of fundamental frequencies and the sums and differences of such frequencies. Normally, overtone and combination absorptions are considerably weaker than the fundamental frequencies and are not of significance when an empiricist interprets an infrared absorption spectrum. There are a few exceptions, such as certain C—H absorptions in the 2 to 3.5 μ section of the near infrared,²⁴ the C—Cl

overtones from the C—Cl₂ groupings at about 1480 cm⁻¹, and the very useful absorption patterns of substituted aromatics³⁷ in the 2000 to 1650 cm⁻¹ range.

The customary tendency for a beginner in empirical infrared spectroscopy is to "over-interpret" a spectrum, trying to interpret and assign too many of the observed absorptions, particularly those of moderate and weak intensity (see Chapter 5).

Symmetry and Selection Rules

The geometrical arrangement in space of the nuclei of the atoms comprising a molecule is known as its *symmetry*. The symmetry of a molecule determines, in large measure, the form of the normal vibrations and the *selection rules* which govern whether any given vibrational mode will absorb infrared radiation (be infrared active) or not (be infrared inactive).

The symmetries possible for molecules to possess were worked out long ago, strictly on the bases of mathematical and geometrical considerations. Schoenflies, e.g., worked them out for his theory of crystal structure. From the symmetry a molecule possesses, one can determine how many of the $3N - 6$ vibrations will be observed in its infrared spectrum. And conversely, if the infrared spectrum is known but not the molecular symmetry, the latter may be largely deduced.

The vibrational selection rules dictated by the symmetry of a molecule determine the spectroscopic activity, i.e., the occurrence or nonoccurrence of any given vibration in the spectrum. These selection rules limit the changes in the $3N - 6$ quantum numbers, v_i , in the following manner:

(1) Only one of the quantum numbers can change during a transition between vibrational levels arising from the emission or absorption of radiation.

(2) The above change, Δv , is $+1$ or -1 .

(3) For vibrations involving no change in dipole moment, Δv must always be zero.

The above rules mean that each frequency observed in the spectrum is identical with the frequency of one of the molecular vibrations. The complete set of vibrational frequencies, however, will not necessarily all appear in the spectrum for those modes to which the $\Delta v = 0$ selection rule applies will not be observed.

Herzberg¹² has considered all the various symmetries that are likely for real molecules and classified their vibrations. From these tables the investigator may determine the spectroscopic activities of the vibrations of molecular structures with which he is concerned. He can say how many of the $3N - 6$ vibrations will be observed in the infrared spectrum solely on the basis of symmetry.

It is important to realize the vibrational selection rules just discussed are based on the following assumptions: the vibrations are harmonic, and the molecules are in the vapor state, free from the interaction effects of neighboring molecules. The practical spectroscopist, however, is most often confronted with molecules in the liquid and solid states. Accordingly, the selection rules are changed, because the simple assumptions on which they are based are not justified.

The major change in selection rules is to allow more than one quantum number v to change during a transition between vibrational levels, and to permit Δv to be 2 or even higher. Overtones and combination tones can now appear in the spectrum as the result of these altered selection rules. These additional bands are, in general, of very weak intensity in comparison with the fundamental vibrations, permitted by the simple selection rules. Significant deviations from the third selection rule above also occur, but only in the infrared spectra of liquids.

The Diatomic Molecule

A diatomic molecule yields an absorption spectrum that shows most of the fundamental features of molecular spectra. It also is the simplest molecule that can undergo a vibrational motion. When a chemical bond as, e.g., in the diatomic molecule $A - B$ is formed, two forces have reached equilibrium: the attractive force between A and B which is predominant at larger ($A \cdots B$) distances and the repulsive force which is exercised most vigorously when the ($A \cdots B$) bond is compressed to less than its equilibrium distance, r_e .

The electronic energy levels of all molecules, including diatomic ones, are dependent on the distance between atoms. The speed of electrons in their orbits is the order of 10^8 cm/sec, while the speed of atomic nuclei undergoing a molecular vibration is at most 10^6 cm/sec and usually slower. An electron moves only about 10^{-8} cm (1\AA) in going from one orbit to another. It thus requires only about 10^{-16} sec for the orbit change. During this time interval the vibrating nuclei move less than 10^{-10} cm, or less than one-hundredth of the internuclear distance. For practical purposes, then, the internuclear distance remains fixed during an electronic transition.

In real diatomic molecules the change in quantum number, Δv , is not restricted to any one value but can have a range of values, a few of these being much more likely than others. The most probable Δv values correspond to the highest intensity bands observed in the spectrum. This method of finding Δv in diatomic electronic spectra is the *Franck-Condon principle*.¹¹

Associated with a given electronic transition is a collection of vibrational bands called a *bund system*. When analyzing such a collection, it is frequently possible to assign a regular series of bands to a single value of

ν' ,¹⁰ and to successive values of ν'' ,* or vice versa. This regular series is called a *progression*. When $\Delta\nu$ is constant, regardless of the values of ν' and ν'' , groups of bands with the same value of $\Delta\nu$ occur together and are called *sequences*.

The emission-band spectrum and the absorption-band spectrum of a molecule can be, and experimentally often are, quite different in appearance. This difference occurs because $\Delta\nu$ may be quite different for transitions beginning in an excited state compared to those beginning in the ground state. Part of this difference is brought about by the means used to excite an emission spectrum, such as an electrical discharge or high-temperature flame.

It is often possible to measure directly and with high accuracy the energy of dissociation (D_e'') of a diatomic molecule from the vibrational analysis of its spectrum. Such becomes possible when the vibrational levels of the ground state can be traced to large quantum numbers. The D_e'' 's of H_2 and Cl_2 e.g., have been determined in this manner.

Vibrational frequencies are hundreds to many thousands of times larger than those of rotation. The frequency of a pure vibrational transition, therefore, differs very little percentagewise from that of the corresponding transition in which both vibration and rotation occur. Consequently every pure vibrational transition is observed in the immediate neighborhood of a collection of vibrational-rotational transitions. The members of the collection differ only in the rotational quantum numbers involved, and the collection is called a *vibration-rotation band*.

The positions of the rotational lines in such a band are given to a first approximation for a diatomic molecule by

$$\sigma = \sigma_{\text{vib}} \pm 2JB \quad (1-13)$$

where σ_{vib} = the cm^{-1} corresponding to the pure vibrational transition and J = the only quantum number on which the rotational energy of linear and spherical top molecules depends. J takes the values 1, 2, 3, . . .

The *P* branch, the left-hand side, of a vibration-rotation band in infrared absorption is given by the *minus* sign corresponding to a selection rule $\Delta J = -1$; the *R* branch, the right-hand side, by the *plus* sign, $\Delta J = +1$. With J restricted to integers higher than zero, Equation (1-13) yields no frequency corresponding to the pure σ_{vib} . Because $\Delta J = \pm 1$, there is a gap in the center of the vibration-rotation band. Bands with this central gap are called *parallel bands*. It appears in all molecules in which the dipole moment vibrates parallel to the molecular bond. In diatomic molecules this is the only way the moment can vibrate, so vibration-rotation

*Upper energy states are by convention designated with a single prime and lower energy states with a double prime.

spectra of all diatomic molecules which absorb infrared will show the central gap.

Linear polyatomic molecules undergo certain vibrations during which the dipole moment vibrates in a direction perpendicular to the line of the molecule. Since the rotational selection rule is then $\Delta J = 0, \pm 1$, the *P* and *R* branches are joined by a third, the *Q* branch, for which $\Delta J = 0$. The various members of the *Q* branch all have the same frequency, that of pure vibration, since there is no change in rotational energy when *J* does not change. Accordingly, the *Q* branch occurs in the center of the band. A band with *P*, *Q*, and *R* branches is called a *perpendicular band*.

The vibration-rotation bands discussed above apply only to small molecules in the vapor state. In the liquid and solid phases, the rotational levels are smeared out and only vibrations are of practical importance.

The diatomic molecule A-B can undergo only a str vibration along the bond between atoms A and B. One can consider A and B as two point masses or balls, with the mass of each proportionate to its atomic mass, connected by a spring of strength proportionate to the chemical forces holding atoms A and B together as a molecule. A str vibration then occurs if the spring is compressed and then the whole left on its own.

If the stretching or oscillation back and forth periodically is moderate, then Hooke's Law is obeyed for the simulated masses and spring just as it is to a reasonable approximation for a real diatomic molecule. Thus

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{f}{u}} \quad (1-14)$$

where

ν = the str vibrational frequency

c = the velocity of light

f = the forces holding the atoms together, the *force constant*

u = the reduced mass, defined as:

$$u = \frac{m_A \cdot m_B}{m_A + m_B}$$

where m_A and m_B are the masses of atoms A and B, respectively.

Since many molecular vibrational frequencies are predominantly those of groups of two, three, or other small number of adjacent atoms within a molecule, and are reasonably independent of the chemical makeup of the rest of the molecule, one can use Equation (1-14) above to calculate approximately the str vibration for two unlike atoms.

Substituting in Equation (1-14) the values for π and c , a practical, useful form results.

$$\nu = 1307 \sqrt{\frac{f}{u}} \text{ cm}^{-1} \quad (1-15)$$

where

f = a pure number

and

u = atomic mass units.

When H is one of the two atoms involved in a diatomic grouping within a molecule, owing to its mass of 1, there is usually a great mass difference between the two atoms. For example, in C—H the masses are approximately

12 : 1. The reduced mass is thus $u = \frac{12 \cdot 1}{12 + 1} = \frac{12}{13}$

Then with reasonable approximation, one can say $\frac{12}{13} \cong \frac{12 \cdot 1}{12} \cong \frac{12}{12} \cong 1$

i.e., $\frac{m_A \cdot m_B}{m_A + m_B} \cong \frac{m_A \cdot m_B}{m_A}$ and Equation (1-15) reduces to

$$\nu = 1307 \sqrt{\frac{f}{m_A}} \text{ cm}^{-1} \quad (1-16)$$

And similarly for other atoms of large mass difference or for C—X where "X" indicates any real atom that can form a chemical bond with carbon.

Values of the force constant, f , have been determined to be about 5×10^5 dynes per cm for single bonds, about 10 for double bonds, and about 15 for triple bonds. With these approximate values, one can calculate the frequency of a str vibration to give him the spectral region in which to look for a "new" absorption band arising from a grouping not yet correlated and listed on the several infrared spectra-chemical structure charts^{8, 21} available (see chart in Chapter 6). Very few str vibrations remain uncorrelated.

Calculations of the important and widely useful hydrogenic str frequencies yield good approximations to experimentally observed values. Consider the C—H str vibration. Substituting the appropriate values in Equation (1-16),

$$\nu = 1307 \sqrt{\frac{5}{1}} \cong (1307)(2.236) \cong 2925 \text{ cm}^{-1}$$

In methane, the C—H absorption is observed at about 2915 cm^{-1} , which is in good agreement with the approximate calculation. Similar approximate agreement between calculated and observed results is obtained, e.g., for the str vibrations of C=O, C≡O, and C≡N in simple molecules such as methyl alcohol, acetone, and hydrogen cyanide, respectively.³

Calculations using Equation (1-15) are naturally of most value when the two atoms have large mass difference, as in the case of C—H treated above, and when the remainder of the molecular structure exerts little, or

practically no, influence on the vibration being studied. Atom—H str vibrations, therefore, are among those most thoroughly studied to date, and studies thereon have solved many molecular structure problems.

Such good agreement between calculated and observed values, as obtained for hydrogenic str frequencies, will not always prevail. Suppose the location of the C—F str frequency in CH_3F were not known—it is, of course. Substituting the approximate values in Equation (1-15),

$$\nu = 1307 \sqrt{\frac{f}{\mu}} = 1307 \sqrt{\frac{5}{7.4}} = 1307 \sqrt{0.68} = (1307)(0.825) = 1080 \text{ cm}^{-1}$$

since

$$\mu = \frac{12 \cdot 19}{12 + 19} = \frac{228}{31} = 7.36$$

The spectroscopist confronted with finding this "new" C—F absorption would scan the 2 to 15μ region absorption spectrum of CH_3F gas and look in the 1100 cm^{-1} region for an absorption band.

He would observe a very strong absorption at 1048 cm^{-1} . The 3% difference between observed and calculated values would raise doubt in his mind. Let it be stated at once—an unfavorable example has been used. The mass of F, 19, is not too far different from that of C, 12. Single bonds, in general, such as the C—F bond, occur over wide frequency ranges because of their sensitivity to interactions with neighboring groups, in contrast to the narrower frequency ranges in which double bond groupings occur, and the even narrower frequency ranges in which triple bond groupings occur. Furthermore, of all the halogens, fluorine shows the greatest frequency range variation, since among other properties it has the smallest mass and size of the halogens.

The fundamental C—X str vibrations (known as ν_3) of the methyl halides¹³ are:

Halide	$\nu_3(\text{cm}^{-1})$	$\Delta\nu_3(\text{cm}^{-1})$
CH_3I	533	
CH_3Br	611	78
CH_3Cl	732	121
CH_3F	1048	316

While the increase in frequency upon going from CH_3I to CH_3Br to CH_3Cl is normal and expected with the decreasing mass the basis, the very large change ($\Delta\nu_3$ above) on going from CH_3Cl to CH_3F is much greater than expected. The reason for this is that it is not strictly accurate to call 1048 cm^{-1} the C—F str frequency of CH_3F . Actually the ν_3 and ν_2 (symmetrical C—H bending) vibrations of CH_3F interact with each other, which results in a greater $\Delta\nu_3$ between CH_3Cl and CH_3F than would be predicted. Hence,

the 1048 cm^{-1} vibration cannot be attributed solely to one functional grouping in the molecule. This is an example of the limitations of the concept of group frequencies. A frequency will remain reasonably constant in a series of molecules containing the same functional group(s), and can be assigned to that group only if no other frequency belonging to a normal mode of the same species is in the same frequency range.

Because of its very strong dipole, $\text{C}=\text{F}$ shows a very large change in dipole moment during its str vibration and thus gives rise to very intense infrared absorption. Occasionally, the spectroscopist will need to use infrared for identification or molecular structural purposes on $\text{C}=\text{F}$, $\text{C}=\text{Cl}$, C -halogen groupings in molecules, but infrared techniques are not ordinarily needed for the determination of the presence or absence of halogens, particularly in organic molecules. The Beilstein³³ and other appropriate analytical techniques will suffice.

Equation (1-15) shows that the absorption frequency for a specific pair of atoms depends on the masses of the atoms and the forces binding them together. In addition, the geometrical arrangement in space of the atoms comprising the molecule is the third important factor. Thus, all types of geometrical isomers can be distinguished from one another by their infrared spectra, with the exception of optical enantiomorphs. Optical isomers are indistinguishable by infrared. One still needs to distinguish such by their varying degree of rotation of plane polarized light. Polymorphic forms of both organics and inorganics are distinguishable by infrared. Thus, the various shades of copper phthalocyanine blue have been distinguished and several new polymorphic forms of this pigment were first uncovered by infrared techniques.²⁶

The small variations observed from spectra in the frequency positions of maximum absorption for molecules of the same chemical class, such as esters, e.g., enable the spectroscopist to use the exact frequency of maximum absorption(s) empirically to tell not only that a specific atomic grouping is present, but also often to determine something about the structural relation of this grouping to the remainder of the molecule. For example, the ester carbonyl grouping in esters lacking $\text{C}=\text{C}$ unsaturation (saturated esters) normally absorbs in the infrared from about 1750 to 1725 cm^{-1} (5.71 to 5.80μ), while for esters having $\text{C}=\text{C}$ unsaturation, the range is from about 1730 to 1715 cm^{-1} (5.78 to 5.83μ).

The small variations cited above arise from small variations in f and u . That such do occur gives rise to the careers of empirical infrared spectroscopists.

Having determined the absorption frequency for a given atom pair experimentally, the force constant, f , or the chemical binding energy between the vibrating atoms can often be calculated.

Numerous studies reported in the literature show that, in general, the larger the value of f , the shorter the equilibrium distance between the atoms of interest. As previously indicated, normally the force constants for triple bonds are greater and the interatomic equilibrium distance less than for double bonds, and similarly when the comparison is extended to single bonds.

The reader has now been given some idea of the theoretical justification for the observed fact that certain atomic pairs and groupings yield absorption bands consistently in a well-defined region of the infrared electromagnetic spectrum. It should be emphasized, however, that arbitrarily extracting a portion of a molecular structure and making mathematical calculations thereon, as in Equation (1-15), is *only an approximation* and cannot justifiably be carried to the extreme. The procedure applies only to a small number of existing kinds of atomic vibrations. No one can begin with experimentally determined values of f , equilibrium interatomic distances, and reduced masses, and calculate what absorption spectrum will be observed by this simple-minded approach.

Polyatomic Molecules

For nonlinear polyatomic molecules with $3N - 6$ vibrational motions, one might initially expect a hopeless multitude of unrelated vibrations. The orderliness of nature comes to the rescue. While each of the $3N - 6$ vibrational motions can take place simultaneously and independently, each such motion is related to each other such motion. When the motions represent displacements of atoms from their equilibrium positions by only moderate distances, say less than one-tenth the average interatomic distance, the motions are harmonic, to a good approximation. Every harmonic motion is the superposition of two or more simple vibrations designated *normal vibrations*. Thus, there are $3N - 6$ normal vibrations and $3N - 6$ fundamental frequencies associated with them.

The preceding conclusion can be arrived at empirically or mathematically. Empirically one can construct a mechanical model²⁷ of a molecule, such as benzene, by taking balls whose masses and sizes are scaled to represent the 6C's and the 6H's, arraying them in space according to the geometry of the molecule, and connecting the masses by springs whose strengths are proportional to the forces binding the atoms together into the C₆H₆ molecule. Set the model in motion by appropriate means — striking it a blow in a suitable location is one way — observe its motions with a stroboscopic light of variable frequency, and specific light flash frequencies will be found at which the model atoms appear to stand still. While the motions of the mechanical model present a chaotic pattern, comprehensive observations,

using the variable frequency stroboscope, will show that the N masses, 12 for C_6H_6 , will have $3N - 6$ or 30 frequency motions or *fundamental vibrations* for the C_6H_6 molecule.

Mathematically the same conclusion can be reached, using the same mechanical model of the benzene molecule by the equations of mechanics.³⁰ One would find 30 fundamental vibrations and these are a function of the original knowns — masses, springs, and space geometry.

Benzene has a six-fold axis of symmetry. Rotation of this molecule by 60° , i.e., $360^\circ/p$ where $p = 6$, produces a configuration indistinguishable from the original one. A *point group* is defined as a possible combination of symmetry operations which leaves at least one point unchanged. *Symmetry Operations* are a coordinate transformation that produces a configuration of the nuclei indistinguishable from the original one. Any geometrical figure or object, such as a molecule arrayed in space, may have one or several *symmetry elements*. To each symmetry element there corresponds a symmetry operation. Typical symmetry elements are a plane, center, and axis of symmetry, among others.

Group theory demonstrates that only a limited number of point groups exist and that every molecule must belong to one of these point groups.^{32,34} Benzene, e.g., belongs to the D_{6h} point group. The subscript "h" arises from the fact that there is a horizontal plane perpendicular to the 6-fold axis in benzene. D_{6h} for benzene means that all the C—C bonds are equivalent and that the H atoms are in the plane of the C atoms and in their most symmetrical positions. Numerous investigations, based on both spectroscopic and chemical observations, have shown that benzene does have the point group D_{6h} .¹⁴ This point group allows that of the $3N - 6$ or 30 possible fundamental frequencies of benzene, only 20 can be observed in the infrared. Ten of these are *non-degenerate*, i.e., unique, while ten are doubly *degenerate*, i.e., the latter ten each has another vibration of identical frequency. Thus, $10 + (2)(10) = 30$. Hence, the high geometrical symmetry of benzene reduces the 30 normal vibrations to 20 fundamental frequencies.

Because the D_{6h} model of C_6H_6 has a center of symmetry, absorption bands observed in the infrared spectra should not appear in the Raman spectra* and vice versa.

Actually five strong bands have been observed in the infrared spectra of C_6H_6 . Four of these are fundamental frequencies and one is a resonance

*While Raman spectroscopy⁵ is beyond the scope of this volume, the reader should be aware that Raman complements infrared and the two techniques jointly are a powerful means of unravelling the molecular structures of molecules. The Raman effect is a light scattering phenomenon dependent on a change of polarizability of a molecule. In contrast to Rayleigh scattering in a transparent molecular medium during which no change in wavelength occurs, Raman scattering gives rise to weak new lines of altered wavelength which are characteristic of the scattering medium.

doublet of a fundamental frequency and the combination of two other frequencies.

Using results from both infrared and Raman spectra, only eleven of the twenty fundamental frequencies of benzene have been observed. Because of the high symmetry of benzene, nine of the fundamentals are inactive. Based on assumptions about the forces among the atoms comprising C_6H_6 , E. Bright Wilson³⁵ has derived formulae for all the frequencies. Rigorous agreement between the observed and calculated infrared spectra, however, are not yet completely at hand. C_6H_6 is by no means a "large" molecule from the industrial standpoint. The reader can readily appreciate the necessity for using the methods of empirical infrared spectroscopy for molecules of commercial interest which are often much larger and much less symmetrical than benzene.

Using *real* molecular data — atomic weights, interatomic distances and angles, and chemical binding forces, f , the results from use of the equations of mechanics on a variety of molecules yield molecular frequencies from about 12 to 0.6×10^{13} cps.

Now $\bar{\nu}$, frequency in cycles or waves/sec, the fundamental unit of frequency, can be expressed, as previously noted in Equation (1-3):

$$\bar{\nu}(\text{sec}^{-1}) = c\nu$$

where

ν = waves/cm expressed cm^{-1} and c = the velocity of light.

The region of primary infrared interest extends from about 4000 to 200 cm^{-1} (2.5 to 50 μ) because $\bar{\nu} = 12 \times 10^{13}$ cps for 4000 cm^{-1} and $\bar{\nu} = 0.6 \times 10^{13}$ cps for 200 cm^{-1} , and these are also the frequencies of infrared radiations.

Since 0.6×10^{13} and 12×10^{13} cps are not as convenient to use in everyday spectroscopy as 200 and 4000 cm^{-1} , the frequency unit commonly used is ν , expressed as cm^{-1} or waves/cm.

Since λ (wavelength) $\cdot \bar{\nu}(\text{cps}) = c$ (velocity of light)

$$\nu = \frac{\bar{\nu}}{c} = \frac{1}{\lambda(\text{cm})} = \frac{10^4}{\lambda(\mu)} \quad (1-17)$$

For example, what cps frequency, $\bar{\nu}$, corresponds to 1250 cm^{-1} ?

$$1250 = \frac{\bar{\nu}}{3 \times 10^{10}}$$

$$\bar{\nu} = 3.75 \times 10^{13} \text{ cps}$$

$$\lambda(\mu) = \frac{10^4}{\nu}$$

$$\lambda(\mu) = \frac{10^4}{1250} = 8$$

Thus, a $\bar{\nu}$ of 3.75×10^{13} cps = a ν of 1250 cm^{-1} = a λ of 8μ .

Vibrational Spectra — Classical Treatment

The emission* or absorption of radiation by a molecule occurs when there is a change in its dipole moment during a vibration. While a change of the quadrupole moment or of the magnetic dipole moment may also yield emission or absorption of infrared radiation, the intensities of such are exceedingly small, and they shall be considered zero for this volume.

Molecular Vibration, Dipole Moment Change, and Infrared Absorption. The atoms of any molecule possess a positive or negative charge, owing to their inherent electrical nature. These positive and negative charges can be represented as point charges by concentrating them at their respective electrical centers of gravity. The dipole moment is the vector line between these electrical centers. Since the dipole moment is a vector possessing both magnitude and direction, a change in dipole moment during a molecular vibration can arise from a change in either magnitude or direction. The location of the charges on atoms vary as the atoms undergo their characteristic vibrations. A molecule, therefore, may have one value for its dipole moment at one extreme of a vibrational mode, and a different value at the other extreme. When these two extreme values are different, a change in dipole moment is said to be associated with that characteristic vibration. When these two values are the same, there is no dipole moment change.

Consider the simple linear polyatomic molecule CO_2 with $3N - 5$, i.e., four vibrational modes. Two of these are degenerate, i.e., coincide in frequency, because the two bending vibrations occurring in planes perpendicular to each other require the same energy and therefore have the same frequency. Thus, there are only three fundamentals for CO_2 , as for any triatomic molecule. The fundamental vibrations and the dipole moments in the equilibrium state and in the vibrational extremities are as follows:

In Figure 1-3, vibrational modes designated ν_3 and ν_2 † are accompanied by dipole moment changes and are therefore infrared active, i.e., absorb

*Extensive investigations have been carried out on emission spectra, particularly on gases, but emission is beyond the scope of this volume. The reader is referred to Refs. 7 and 29 at the end of this chapter. For industrial and military uses of infrared emission, see, e.g., Holter, Nudelman, Suits, Wolfe, and Zissis, "Fundamentals of Infrared Technology," New York, MacMillan, 1962. Infrared absorption is far more useful industrially than infrared emission.

†See Herzberg¹⁵ for the conventions used in spectroscopy to denote vibrations as ν_1 , ν_2 , ν_3 , . . . etc.

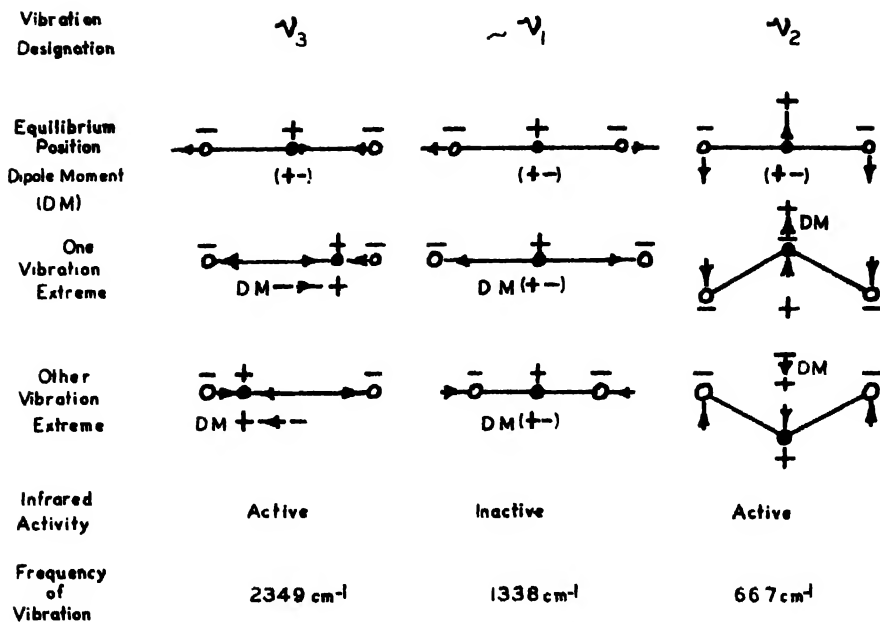


FIGURE 1-3. Fundamental vibrations of CO₂ and dipole moment changes.

infrared radiation. Vibration $\sim \nu_1^*$ shows no change in dipole moment and is therefore infrared inactive, i.e., does not absorb infrared radiation.

The CO₂ molecule at equilibrium has no dipole moment since the charges on the atoms are balanced. More formally, CO₂ possesses no permanent dipole moment because on the average its center of negative charge coincides with its center of positive charge.

How do modes ν_2 and ν_3 absorb infrared radiation? When infrared radiations of the same frequencies as ν_2 and ν_3 impinge on the vibrating CO₂ molecule, one might expect an exchange of energy provided a coupling mechanism is present, just as air acts as a coupling mechanism between two tuning forks of the same frequency. The coupling mechanism is the dipole moment change. The oscillating electric field of the radiation alternates the charge distributions in the manner shown in Figure 1-3 for the change in dipole moment. Thereby the molecule is caused to vibrate, energy is transferred from the radiation to the molecule, and the radiation is absorbed in whole or in part. The vibrational energy gained by the molecule is converted to translational energy through collision with neighboring molecules and the molecule reverts to its initial state ready for

*This vibration has been designated "approximately ν_1 ," but in actuality is a mixture of vibrations ν_1 and $2\nu_2$.

another radiation absorption. The translational energy gained by the molecule is observed as a temperature increase of the sample, which is the basis of infrared heating.

The Harmonic Oscillator Approximation. Because a vibrational motion of a molecule is accompanied by a periodic change in the charge distribution, the dipole moment changes periodically. Therefore, from classical mechanics, the harmonic oscillator approximation applies. The normal or fundamental frequencies are the ones that absorb infrared radiation, since they are the only simple periodic motions occurring. These frequencies are observed in the fundamental infrared region.

Normal vibrations appearing in the infrared spectrum are designated *infrared active*, while vibrations involving no change of dipole moment and which therefore do not appear in the infrared spectrum are designated *infrared inactive*.

In the classical harmonic oscillator approach, only fundamental vibrations are active; overtone and combination frequencies are inactive.

Unsymmetrical molecules yield normal vibrations, all of which are infrared active. Symmetrical molecules may have vibrations which are infrared inactive, but not every symmetrical molecule has inactive vibrations.

It can be shown that the intensity¹⁶ of a fundamental absorption band of a molecule is proportional to the square of the vector representing the change in the dipole moment for the corresponding fundamental (normal) vibration near the equilibrium position of the atoms concerned. Why the C—F group absorption intensity is so very much greater than that of C—H, e.g., is thus readily understood.

Anharmonicity. In the true molecular vibration situation of an actual molecule, the vibrations are not strictly *harmonic*. The deviations from harmonicity are designated *anharmonicity*. When anharmonicity is taken into account, the classical treatment allows overtone and combination vibrations as well as fundamentals, provided, of course, the change of dipole moment criterion is met. Since anharmonicities are quite small, the overtone and combination vibrations and the infrared absorption therefrom will normally be much weaker than the absorptions from the fundamentals.

Vibrational Spectra — Quantum Mechanical Treatment

For small displacements of the nuclei, a molecule may be considered a superposition of harmonic oscillators. The harmonic oscillator approximation dictates that no simultaneous jumps of two or more vibrations can occur, since the oscillators are independent. Thus the selection rule

$$\Delta v_i = \pm 1 \quad (1-18)$$

applies for each normal vibration ν_i . The change in dipole moment criterion must, of course, also be met. When it is met, the wave numbers of the infrared absorptions are then equal to the actual vibrational frequencies. Thus

$$\nu = \omega_i \quad (1-19)$$

where ω_i is the vibrational frequency.

By quantum theory the frequencies of the infrared absorption bands are determined by the differences in energy of the vibrational levels between which transitions take place. Since one wishes to know which transitions occur and with how much intensity, the probability of transitions occurring is required, i.e., *transition probabilities*.

It can be shown that the *vibrational transition probability*¹⁷ is proportional to the square of the following equation. This equation implies that the electronic and rotational states of the molecule can be neglected during a vibration — a reasonably good approximation, as previously discussed.

$$[M]^{v'v''} = \int \psi_v \psi_{v''}^* M d\tau \quad (1-20)$$

where $[M]^{v'v''}$ is the transition moment of the $v' \leftrightarrow v''$ transition with v' representing the upper state and v'' representing the lower state of a transition between these two vibrational levels. And $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions of the upper and lower states, respectively; M is a vector of the dipole moment; the asterisk indicates complex conjugate quantities; and τ is a time factor.

From the vibrational transition probability, the *general vibrational selection rule for the infrared* is that a vibrational transition $v' \leftrightarrow v''$ is allowed only when at least one component of the dipole moment M is the same species as the product $\psi_{v'} \psi_{v''}$. This selection rule does not depend on the vibrations being harmonic.

The general selection rule can also be stated: a vibration of a molecule is infrared active as a fundamental if it behaves with respect to all symmetry operations permitted by the symmetry of the molecule, in the same way as at least one component of the dipole moment.

While selection rules for the infrared can be derived by a treatment which lends itself also to the calculation of intensities, to obtain the absolute intensity requires a direct and accurate determination of the true absorption coefficient. This direct determination has never been made successfully without introducing assumptions with which at least some theoreticians are in disagreement. While progress in this direction is being made, the infrared intensity situation needs further work by the best minds available.

Overtone and Combination Bands. Overtone bands arise from vibrational transitions for which one $\Delta v_i > 1$. While normally much weaker than the

absorption of fundamentals, they may be observed in the infrared by using sufficient thickness of sample layer.

Combination bands arise from vibrational transitions for which several $\Delta v_i \neq 0$. They show intensity properties similar to overtones and also may be observed at sufficient sample thickness.

For transitions in which one vibration changes by two quanta, $|\Delta v_i| = 2$, or two vibrations change by one quantum $\Sigma|\Delta v_i| = 2$, the overtone and combination bands are designated *binary combinations*. Those for which $|\Delta v_i| = 3$ or $\Sigma|\Delta v_i| = 3$ are designated *ternary combinations*, and so on.

Normally ternary combinations are less intense than binary, quaternary weaker than ternary, etc. In a small number of instances, a fundamental vibration may be forbidden, while certain overtone and combination bands involving the same vibration are allowed.

For overtone bands, the lower state is the vibrational ground state. And just as for fundamental vibrations, conclusions as to the symmetry of a molecule can be drawn from the occurrence and non-occurrence of certain overtone absorptions.

A combination band for which the lower state is the vibrational ground state of a molecule is also designated a *summation band*, because its frequency is the sum of the frequencies of two or more fundamentals or overtones.

The spectroscopist should remember that *inactive* fundamentals combined with other fundamentals or overtones may give *active* summation bands. And overtones of certain *inactive* fundamentals may be *active* in the infrared. Furthermore, certain combination bands may be forbidden, even though the fundamentals involved are active. A useful rule is that the lower the symmetry of a molecule, the fewer restrictions there are for both the overtone and combination bands.

For real molecules the vibrations are anharmonic, since the quantized vibrations, although usually small in comparison to interatomic distances, are never infinitesimal. And the concept of normal or fundamental vibrations rests on the assumption of infinitesimally small amplitudes of the vibrations.

Fermi Resonance. Two vibrational levels of a polyatomic molecule belonging to different vibrations or combinations thereof may have approximately the same energy. This phenomenon is designated *accidental degeneracy*.

Fermi⁹ was first to understand this phenomenon with CO_2 , and since then it has been known as Fermi Resonance. The "resonance" leads to "a perturbation of the energy levels." This means the latter interact with each other. This interaction produces a much greater separation of the two vibrational levels concerned than expected. It can be shown that Fermi

resonance can occur only between levels of the same species, i.e., same symmetry type. This rule restricts the occurrence of Fermi resonance to a relatively small number of cases when *symmetrical* polyatomic molecules are under consideration.

A number of molecules have been found to exhibit Fermi resonances. In all such cases, a fundamental vibration ν_i has nearly the same frequency as a first overtone $2\nu_k$ of another vibration or as a binary combination $\nu_k + \nu_l$ of two other vibrations.

Difference Bands. When the initial state is not the vibrationless ground state of a molecule difference bands can be observed in the infrared. For a transition from a singly excited lower state ν_i to a singly excited state with vibration $\nu_k (> \nu_i)$ the frequency of the absorption band is equal to $\nu_k - \nu_i$.

Quantum theory leads directly to a conclusion in agreement with experimental observation in contrast to the classical treatment. Classically, the difference band $\nu_k - \nu_i$ should have the same intensity as the corresponding summation band $\nu_k + \nu_i$, but from quantum theory the intensity of $\nu_k - \nu_i$ would be expected to be much smaller than that of $\nu_k + \nu_i$ because the number of molecules in the initial state is much smaller in correspondence with the Boltzmann factor, $e^{-(h\nu_i/kT)}$.

Selection rules allow, or forbid, a difference band $\nu_k - \nu_i$ when the corresponding summation band $\nu_k + \nu_i$ is allowed or forbidden.

Difference bands are observed in the infrared only where ν_i is small, i.e., generally when the lower state is fairly near the ground state. In such instances the Boltzmann factor is not too small, e.g., difference bands of CO_2 are observed.¹⁸

Another type of difference band occurs when the same low frequency vibration is excited in the upper and lower state in addition to some other vibrations in the upper state. For example, if ν_k is excited by one quantum in the upper state, but not in the lower state, and ν_i is excited both in the upper and lower states by one quantum, a band is obtained as $\nu_k + \nu_i - \nu_i$. Because of coupling of the two vibrations, $\nu_k + \nu_i - \nu_i \neq \nu_k$. Hence, the vibration and the infrared absorption therefrom is observable.

When ν_i is sufficiently small, even bands such as $\nu_k + 2\nu_i - 2\nu_i$ and $\nu_k + 3\nu_i - 3\nu_i$ may have enough intensity to be observed.

Absorption bands of the types just described have been observed by Herzberg, Patat, and Verleger,¹⁹ Zumwalt and Badger,³⁸ and others.

It is of important help in molecular structural analysis by infrared that the wave number of a difference band $\nu_k - \nu_i$ is *exactly* the difference between the wave numbers of ν_k and ν_i even with anharmonicity taken into account, while the wave number of the summation band $\nu_k + \nu_i$ is *not exactly* the sum of wave numbers ν_k and ν_i . Thus, observation of infrared difference bands supplies useful *combination relations*, which may serve as

checks on the vibrational analysis. Difference bands may be used accurately to determine the wave numbers of fundamentals that cannot be observed directly, while summation bands yield only approximate values. If, e.g., ν_k is known, then from observation of $\nu_k - \nu_l$, ν_l is obviously then determined.

Vibration Bands — Fine Structure. While vibration has been considered up until this point as an independent motion of a molecule, in real molecules rotation takes place simultaneously with vibration. This gives rise to the fine structure of infrared vibration bands. Very accurate and reliable information about the structure of small molecules and some larger ones of high symmetry can be garnered from investigation of this fine structure in specific molecules. Such investigations can result in determinations of moments of inertia, inter-nuclear distances, and valence angles — in many cases with greater accuracy than any other method.

Wilson³⁶ has pointed out, however, that recent work suggests that bond length determinations have an accuracy no better than $\pm 0.01\text{\AA}$ in contrast to the $\pm 0.001\text{\AA}$ accuracy spectroscopists thought they had been achieving.

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CHAPTER

2

Survey of Practical Information

David N. Kendall

INFRARED SPECTRA OF MOLECULES IN DIFFERENT PHASES

Viewing the 5000 to 667 cm^{-1} (2 to 15 μ) rock salt region infrared spectra of the vast majority of molecules, which can be conveniently obtained in gas, liquid, and solid phases and scanned separately in each such phase, one is struck by the general over-all similarity of the spectra. Such general conformity is to be expected, since for any given molecule the forces holding the atoms together are very roughly 20 times greater than the forces holding the molecules together. One expects and observes, however, some differences, as between the spectrum of the same molecule in the gaseous, liquid, and solid states. The gas phase spectrum will show rotational fine structure because molecular interaction effects will be at a minimum. The liquid phase spectrum will show very little rotational structure, and molecular interaction effects will be more pronounced. The solid phase spectrum will show practically no rotational structure, molecular interaction effects will be at a maximum, new absorption bands will appear, and certain previously observed single absorptions will be split into two or more absorptions.

The Vapor Phase

The infrared spectrum of a molecule in the vapor state can yield the maximum quantity of information about its molecular structure. This is true because in the vapor phase a molecule is free to rotate as well as vibrate, since molecular interaction is at a minimum. An information-packed vibration-rotation spectrum results from scanning a molecule in

the vapor state. The practical utility of gaseous spectra is not, however, as great as might be predicted from the aforementioned statements. In fact, vapor spectra are so rich in broad, often overlapping vibration bands, upon which are superimposed numerous narrow rotational bands, that qualitative analysis is normally more readily carried out on condensed-phase spectra. This is not to say the spectroscopist cannot identify individual compounds and mixtures thereof using spectra obtained in the vapor phase. He can and does. But gaseous state spectra are not the ones of choice, when there is a choice, for qualitative analysis.

Quantitative analysis in the vapor phase is made difficult by the fact that the observed absorbance is a function of both the partial pressure of the absorbing gas and the total gas pressure. A "pressure-broadening" phenomenon is observed as the total pressure increases, even at constant partial pressure of the absorbing gas. The half-width of a rotation band increases as the total pressure increases, owing to the increased molecular collision frequency and severity. Accordingly, quantitative analyses in the gaseous state have to be done at constant total pressure to be meaningful. Very inaccurate "results" will be obtained if this criterion is neglected.

The recent wedding of gas chromatography and infrared spectroscopy has increased the usefulness of both techniques.⁹¹ Vapor phase chromatography (VPC or GC) is a powerful separatory procedure but weak as an identification technique. Infrared spectroscopy is difficult and largely impossible on a ten-component mixture, for instance, but it is a powerful identification tool for a single compound or a few-component mixture. Currently available commercially is a combined VPC-IR instrument designed to complement the two techniques. An identifiable 2 to 15 μ spectrum of a component 0.15 microliters (μ l) in size, e.g., can be produced in 45 sec; 0.03 μ l in size (say 30 μ g of acetone) in 3 min. "Light Pipe" gas cells, maintained at column temperature to prevent sample condensation, accept effluents directly from the chromatograph. Source energy is focused on one end of the gas cell; energy emitted from the other end is focused on the infrared spectrometer entrance slit. A duplicate of the sample tube (cell) is mounted in the reference beam and carrier gas is passed through it to balance the system. A hot wire detector is mounted just in front of the entrance to the sample tube to indicate when the component of interest has reached the absorption tube. Scale expansion 1-10X (see Chapter 3) increases the facility with which a minimum amount of a component can be identified.

The commercial marriage of VPC and IR was predictable, based on the earlier engagement announced by Bird.¹⁹ He used an internally reflecting micro gas cell in which the GC fraction was first condensed and then re-vaporized for subsequent analysis.

Both qualitative and quantitative analyses of individual infrared-absorbing gases and mixtures of these gases can be successfully carried out by infrared. Since the major components of air (N_2 and O_2) do not show specific infrared absorption, infrared-absorbing impurities in the atmosphere can be scanned and identified. Vapor phase spectra can also be conveniently used to identify the solvent systems present, e.g., in unknown resinous solutions and paints. Such volatiles can readily be entered into a previously evacuated gas cell.

The ultimate sharpness and narrowness of the individual rotation bands of vapor phase spectra make them very useful in testing or demonstrating the resolving power of a spectrometer as well as in frequency calibration.⁴³ Light gases such as NH_3 , CO_2 , H_2O , CH_4 , and HCl are most used for these purposes with NH_3 the favorite for testing resolving power.

Owing to the roughly thousand-fold difference between vapor and liquid densities, path lengths for vapor spectra will normally be a thousand-fold greater than for liquid spectra (see Chapter 4).

The Liquid phase

While generally no qualitative differences, with the exception of lessening of rotational structure, are observed in going from the gaseous state spectrum to the liquid state spectrum, there will normally be relatively minor frequency shifts in the positions of the absorption bands. These arise because the vibrating molecule is now surrounded by like neighbors which can influence its frequencies. Intermolecular effects such as dipole-dipole attraction or molecular association can occur.

One observes, e.g., a decrease in frequency from 1742 to 1718 cm^{-1} for the $C=O$ str vibration, as between acetone vapor and acetone liquid. Most of this frequency shift probably arises from the attractive forces between

the individual $\begin{array}{c} + \quad - \\ \diagup \quad \diagdown \\ C=O \end{array}$ dipoles leading to loose associations of separate molecules linked in chains by electrostatic forces.⁸ Each positive charge induces a small additional negative charge in the oxygen atom of the neighboring acetone molecule. Thus an increased contribution results from

the resonance form with $\begin{array}{c} + \quad - \\ \diagup \quad \diagdown \\ C \quad O \end{array}$ structure. The bond lengthens (more single bond character) and the $C=O$ frequency decreases.

It is well known that carboxylic acids exist in dimeric form because of the very strong hydrogen bonding between the carbonyl and hydroxyl groupings of the two molecules. Since this dimeric tendency persists to some extent even in the vapor state and in dilute solution in certain solvents, the change in carbonyl and hydroxyl frequencies from vapor to liquid phase

is abnormal. Liquid phase carbonyl frequencies can be 50 cm^{-1} lower and hydroxyl frequencies as much as 500 cm^{-1} lower than vapor phase ones. Accordingly, the infrared spectra of carboxylic acids are usually scanned in the liquid or solid states where only dimers or higher polymers are observed.^{29,83}

Solutions

Scanning materials in solution in inert, nonpolar solvents offers the spectroscopist a similar environment for his vibrating molecules, important to drawing valid correlations between vibrational frequencies and molecular structure. By using separate solutions of an organic material in CCl_4 and CS_2 , e.g., at about 10% weight by volume (*w/v*) concentration and scanning in an approximately 0.1 mm sealed cell, one can cover the 4000 to 450 cm^{-1} (2.5 to 22.2μ) spectral range to yield spectra of convenient intensity with minimal absorption by either solvent. CCl_4 is employed from 4000 to 1325 cm^{-1} ; CS_2 from 1325 to 450 cm^{-1} . Potts⁷⁶ presents a comprehensive account of the CCl_4 - CS_2 technique.

For materials insoluble in the above solvent combination, other solvents or solvent combinations can be used, provided they have the requisite solubility and infrared transparency. In general, solvents containing no, or minimal, hydrogen, and of small symmetrical structure, show the greatest infrared transparency. Many times only a limited infrared region is of interest, say the $\text{C}\equiv\text{N}$ absorption range from 2200 to 2400 cm^{-1} . In such instances it is only necessary that the solvent employed be nonreactive with respect to nitrile groups and transparent in the region of interest.

A number of cases of solvent-solute interaction are known. Such will normally be mild when nonpolar solvents are used but can be severe with polar solvents. It is thus of critical importance that spectral comparisons be made on solutions of the same concentration and cell path length. Otherwise valid molecular structure conclusions cannot be drawn. Employing a set of such standard conditions gives two added bonuses: one develops a feeling for the relation between band intensity and molecular structure useful in spectral identification of unknowns, and quantitative as well as qualitative analysis can be made using the same spectrum.

Spectral comparisons should be made among various known and unknown materials only on spectra obtained in the same phase under the same conditions of concentration, pressure, temperature, solvent, etc., and scanned using the same instrumental variables. This is a general rule of paramount importance to carrying out valid empirical studies in spectroscopy.

Materials will probably always exist for which no adequate infrared transparent solvent or solvent combination can be found. Obviously, solu-

tion techniques are not applicable and other methods must be used (see Chapter 4).

The Crystalline Phase

Since a crystal is a three-dimensional periodic array of atoms, the symmetry of its building unit, the unit cell, will be different from the symmetry of the individual molecules, which together make up the unit cell. Accordingly, a crystalline solid gives rise to vibrations characteristic of the symmetry of the unit cell called *lattice vibrations*, as well as vibrations characteristic of the individual molecules of which the unit cell is comprised. These vibrations can, in certain cases, couple with each other, thus giving rise to new vibrations which are observed in the crystalline state spectra. Thus, absorptions not observed in the gaseous or liquid state will be observed in the crystalline state.

Molecules can exist in different polymorphic forms in the crystalline state. Such polymorphic forms can be differentiated by infrared, as well as x-ray techniques, for both organics and inorganics. The infrared procedure⁵⁵ is more sensitive to small percentages of one polymorphic form in the presence of other such forms and can detect polymorphs having amorphous regions to which the x-ray technique is insensitive.

Certain chemical treatments can change one polymorphic form of a substance into a different polymorphic form. Temperature changes and sometimes pressure changes can bring about such a solid state transition. The spectroscopist must continually be aware of this, whenever he is working on problems involving the solid state. A true case of polymorphism is easily distinguished by infrared: if identical spectra are obtained for two substances in solution in a solvent, yet their solid state spectra are different, then the "two substances" are different polymorphic forms of the same chemical.

The isolated-molecule frequencies are generally the most noticeable ones, even in the spectrum of a crystalline solid. The new bands observed, and other spectral changes from the spectrum of the isolated molecule, depend for their intensity upon the degree of coupling between the molecules in the unit cell and the coupling between unit cells. These forces are many times less than intramolecular forces.

Infrared spectra can reveal various valuable types of information on solids, supercooled liquids, polymeric materials containing both crystalline and amorphous regions, and both inorganic and organic semiconductors.

Since infrared spectrometers grating instruments even more than prism instruments — produce radiation which is partially polarized, intensity variations in the absorption spectrum are observed when a crystalline sample of uniform thickness is rotated in the sample beam of the instru-

ment. To enlarge this effect, one can irradiate a specimen with radiation polarized at different angles, observe the intensity variations produced in the absorption spectrum, and gain information as to the orientation of the sample under study. Such information can be uncovered because crystal phase absorptions are anisotropic, since the molecules of a crystal are fixed in space in a limited number of definite orientations, sometimes even in one unchangeable orientation.

A supercooled liquid can be distinguished from a true solid. The former will show no more absorption bands than the liquid itself; the latter will have new bands as compared to its liquid state spectrum. Crystallinity studies of polymers (see Chapter 8) are made possible because most such materials are comprised of mixtures of varying degrees of crystalline regions and amorphous regions. Transformations from amorphous (supercooled) to crystalline phases can thus be followed by infrared absorption, and the degree of crystallinity of a number of important polymeric materials in use as resins and fibers can be determined.

In inorganic and organic semiconductors, observation and examination of their spectra can reveal valuable information about the extent and type of electron mobility and electron localization in the chemical structure of these semiconductors. While nonpolar saturated molecules show a minimum coupling between internal vibrational modes and unit lattice modes, ionic and polar unsaturated structures show considerable coupling in the solid state. Thus the doping of semiconductor-type metals, such as germanium, to render them semiconductive in controlled ways, is amenable to evaluation and product control through use of infrared spectroscopy.

Adsorbed Molecules

Both physical adsorption and chemical adsorption (chemisorption) can be profitably studied by infrared spectroscopy. While much has been accomplished, the potential importance of this adsorption field in a time of stereospecific catalysts and stereoregular polymers is immense.

Physical Adsorption. Terenin and colleagues^{60,94,95,96} made the first systematic studies of adsorption phenomena by infrared. They showed, using gases adsorbed onto plates of silica gel and porous glass, that it was misleading to consider the silica surface as solely that of an oxide. By studying hydroxyl absorptions (first overtone) they observed absorption bands of hydroxyl groups attached to the surface by chemical bonds. McDonald^{66,67} and others have shown that differently prepared silica surfaces contain different numbers of hydroxyls; these are differently distributed over the surface; they may occur in isolation on the surface, in adjacent pairs or groups, and possibly as hydroxyl pairs attached to the same silicon atom.

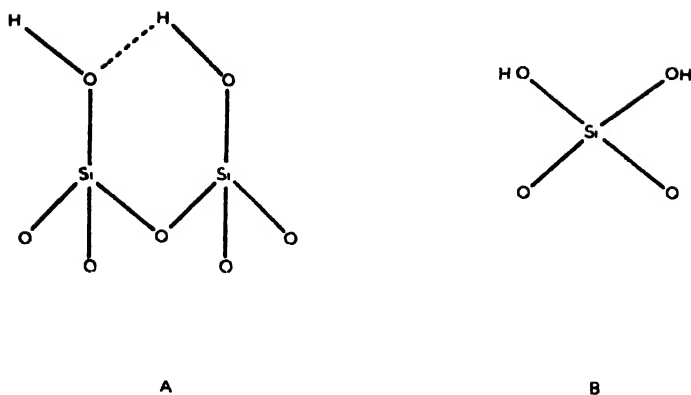


FIGURE 2-1. Hydroxyls on silica surfaces; (A) Adjacent pairs, (B) Two on same silicon.

Yates⁹⁷ *et al.* found, from study of the absorption spectrum of ammonia physically adsorbed on cleaned glass,* that the ammonia nitrogen was strongly hydrogen bonded to surface hydroxyl groups. The broad hydroxyl absorption was observed with a center at about 2900 cm^{-1} . The shift from a normal hydrogen bond which occurs about 3333 cm^{-1} is a measure of the great strength of the bond formed. Through conventional adsorption measurements, they found this broad band could be detected at a fractional coverage of $1/70$ of a monolayer.

Infrared spectra can provide direct evidence for molecular distortions by surface forces which cause infrared selection rules to become inoperative. In methane, e.g., the bond str vibration in which all four hydrogens are moving in phase either toward or away from the carbon atom is infrared inactive. It is not observed in the infrared because the dipole moment does not change during the vibration. Its frequency is known, however, from Raman spectra. Sheppard⁸² and Yates studied the infrared spectra of methane physically adsorbed on porous glass in the C-H str region. Necessary to the study was the successful construction by Yates of a cell which could be heated to 350°C to remove physically adsorbed water, then cooled to near liquid-air temperature in order to yield sufficient adsorption by the volatile methane. They observed an absorption band at 2899 cm^{-1} , only 18 cm^{-1} distant from the gas phase frequency of methane which is normally not observed in the infrared for the reason described above. Evidently surface forces distort the strict tetrahedral symmetry of methane, causing the selection rule to become inoperative and the 2899 cm^{-1} band

*To obtain useful results the porous glass has to be freed from the water and hydrocarbon molecules, normally physically adsorbed on the surface, by heating *in vacuo* up to 300 or 400°C .

to appear. This latter absorption band is thus a direct result of interaction between the adsorbed molecule and the surface.

Infrared evidence has been obtained for rotational motions by molecules physically adsorbed on surfaces of solids where the adsorbed molecule is small and symmetrical.⁶⁵ The evidence resides in band-width phenomena. For methyl bromide adsorbed on porous glass, the infrared spectrum of the surface hydroxyls shows that the molecules are held to the surface by $O-H \cdots Br$ hydrogen bonds. Accordingly, it can be presumed that there is rotation about the $C-Br$ bond axis itself, but not about axes perpendicular to this.

Chemisorption. Chemical adsorption on surfaces produces greater spectral changes than physical adsorption, since new surface species are formed. The pioneering work in chemisorption was that of Eischens,²⁵ Francis, and Pliskin who observed spectra of carbon monoxide adsorbed on metal particles when the latter were smaller than the wavelength of the radiation and were separated from each other by a transparent support such as high-area powdered silica. Their spectra showed that some of the carbon monoxide was adsorbed linearly to a single metal atom and some in a bridged form to a pair of metal atoms. Later Yang⁹³ and Garland showed that a proportion of the carbon monoxide molecules may be adsorbed in pairs on the same metal atoms.

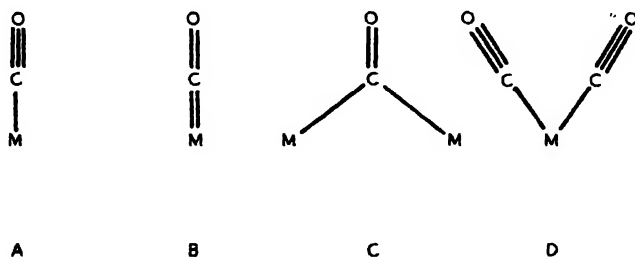


FIGURE 2-2. Carbon monoxide adsorbed on metal; (A) or (B) To a single metal (M) atom, (C) To a pair of metal atoms, (D) Two molecules on one metal atom.

Clark²² and Sheppard studied spectra from propylene and methylacetylene chemisorbed on silica-supported platinum in the 3000 cm^{-1} region. For the initially adsorbed species from propylene, they assigned bands at 2980 and 2850 cm^{-1} to the saturated $C-H$ of the CH_3-C group. Upon hydrogenation of the surface species, a considerable over-all intensity increase was observed. This suggests that more than one additional $C-H$ bond has been formed. These investigators conclude that the initial species very likely were formed through a dissociative mechanism rather than by an

associative mechanism. The spectrum of the hydrogenated species resembled that of an isopropyl group. Analogous spectra were obtained from butene-1 and *cis*-butene-2 adsorbed on silica-supported platinum.

The infrared spectrum of the initially adsorbed species from methylacetylene suggested the presence of some $\equiv\text{CH}$ groups (weak 3015 cm^{-1} band) and that the surface species contained less than one methyl group per C_3 -unit (lack of a strong band near 2970 cm^{-1}). The possibility of several different initially adsorbed species arose. Upon hydrogenation, a methyl-rich species which proved to be an isopropyl group was observed by infrared.

Considerable caution is required in drawing conclusions from chemisorption infrared spectra since slight differences in experimental technique can cause spectral differences even on the same gas-oxide supported metal system. These differences are more apparent than real, however.

Because of their important industrial applications, nearly all of the useful infrared studies of adsorption on metals have been carried out using oxide-supported metal samples. The infrared approach has been the only technique capable of giving helpful direct information about the chemical structure of surface species for gases such as carbon monoxide, and the hydrocarbons propylene, methylacetylene, and the like. Considerable further development is desirable and should prove fruitful.

TYPES OF MOLECULAR VIBRATIONS

Spectroscopists classify vibrations of molecules as to type to facilitate understanding of where they will be observed in the infrared region, how the location and intensity of their absorption bands will be affected by substitution of atoms, and the effect neighboring atoms and atomic groups will produce on these vibrations.

Not all types of persistent vibrational motions produce useful group frequencies. For discussion of those which do, the reader is referred to Chapter 6.

Str Vibrations

A stretching (str) vibration is the back and forth motion along the valence bond of two or three atoms. The $\text{C}-\text{H}$ str in chloroform, e.g., can be represented as $\text{>C} \begin{smallmatrix} \leftarrow \\ \rightarrow \end{smallmatrix} \text{H}$. The small hydrogen mass has by far the greater movement as compared to the twelvefold heavier carbon mass. For a carbonyl grouping, the str vibration involves more nearly equal movement by both atoms, $\text{>C} \begin{smallmatrix} \leftarrow \\ \rightarrow \end{smallmatrix} \text{O}$, and for a nitrile grouping the movement of each atom is

nearly the same because of the closeness of the two masses $\text{—}\overset{+}{\text{C}}\equiv\overset{-}{\text{N}}$. Depending upon the bonding, str vibrations are called single bond str, double bond str, etc. The greater the multiplicity of the bond, the higher is the force constant and thus the higher is the vibration frequency.

When there are two like atoms bonded to the same central atom, as $\text{—CH}_2\text{—}$, there are two str motions. When the two like atoms move along their respective valence bonds in phase, the str is called "symmetric" and when out of phase the str is called "asymmetric." The symmetric and asymmetric str frequencies of a $\text{—CH}_2\text{—}$ grouping are only of slightly different frequency.

When three like atoms are bonded to the same central atom, as in NH_3 or $\text{CH}_3\text{—}$, there are three str motions. One of these is symmetric with all three like atoms moving in phase, and two are asymmetric with the three like atoms out of phase in two different ways. The two asymmetric str vibrations have the same vibrational energy and frequency and are therefore degenerate, giving rise to only one absorption band. The symmetric and asymmetric str frequencies are again of only slightly different frequency. It should be noted, however, that the frequency of absorption of a lone hydrogen attached to a saturated carbon is different from the two str absorptions of a $\text{—CH}_2\text{—}$ group which are in turn different from the two observed str absorptions of a $\text{CH}_3\text{—}$ grouping. Sodium chloride prism resolution, poor in the 3μ region, shows only a doublet when the three groupings mentioned above are all present. It takes the much higher resolution of a grating or a LiF prism to resolve these absorption bands.

One specialized type of str vibration is the so-called breathing vibration. This is a completely symmetric str vibration usually found in ring compounds.

Bending Vibrations

A bending vibration is a motion across the valence bond between atoms. A vibration is classified as bending if no more specialized description is useful or possible. Very often bending vibrations can be further classified more meaningfully into deformation, wagging, rocking, or twisting.

Deformation Vibration. This is a bending-type vibration which produces changes in the angles between the atoms in the structure group concerned.

Internal deformations are those in which the angle of the atomic grouping

itself changes as in $\text{M} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \quad \updownarrow \\ \diagdown \quad \diagup \\ \text{H} \end{array}$. Skeletal deformations are vibrations in which

the changes in angle are slight because the vibrations are tightly coupled to motions of other atoms.

Out-of-plane deformations are bending vibrations in which the motion is perpendicular to a planar structure, such as aromatic or ethylenic. In-plane deformations are bending vibrations in which the motion is strictly in the plane of a planar structure, such as aromatic or ethylenic.

The out-of-plane hydrogen deformation vibrations, e.g., of variously substituted aromatics are of great usefulness in quantitative analyses, as well as in determining the position of substituents on aromatic rings.

Wagging Vibration. This is a bending-type vibration in which the atomic grouping concerned undergoes no internal changes of angle but moves as a rigid unit with respect to the remainder of the molecule. Wagging is thus a swinging back and forth in a plane perpendicular to the molecule's symmetry plane.

Rocking Vibration. This is a bending-type vibration similar to the wagging type except that the atomic grouping concerned swings as a unit back and forth in the symmetry plane of the molecule.

Twisting Vibration. This is a bending-type vibration similar to the wagging type except that the atomic grouping concerned, as a whole, rotates back and forth around the bond which serves to join it to the rest of the molecule.

GROUP FREQUENCIES

As pointed out in Chapter 1, many of the vibrational frequencies of a molecule are predominantly those of very small groups of atoms within the molecule, and these frequencies are characteristic of these groups of atoms no matter in what molecules they occur. These *group frequencies* can be used by the empirical spectroscopist to identify the type and class of compound exemplified by an infrared absorption spectrum or to unravel the number and class of components present in a mixture. From a short preliminary look at the spectrum of an unknown, the experienced spectroscopist can usually decide whether he is confronted with organic or inorganic materials or both, the principal functional groups present in the unknown, and whether it is probably monomeric or polymeric. The reader is referred to Chapter 5 for a general procedure to follow in qualitatively interpreting infrared spectra.

Once the type and class of compound(s) has been deduced, detailed comparisons against known spectra suggested by the preliminary interpretations are carried out until the unknown is identified to the extent possible by infrared.

Empirical correlations of spectra with structure of numerous known compounds together with the vibrational analysis of simple molecules has shown that certain atomic groups such as $\text{O}-\text{H}$, $\text{N}-\text{H}$, $\text{C}-\text{H}$, $\text{C}\equiv\text{O}$,

$\text{C}\equiv\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$, COO^- , vinyl, etc., give rise to absorption bands in specific narrow regions of the infrared spectrum.

The carbonyl group $-\text{C}-$, e.g., will absorb strongly in the range from



2150 to 1620 cm^{-1} , but the precise absorption frequency within that range depends on whether the substance scanned is an anhydride, lactam, acid chloride, ester, acid, ketone, carboxylic acid salt, etc. The carbonyl groupings of phthalic anhydride, e.g., absorb at 1845 and 1775 cm^{-1} ; those of 1, 4-dihydroxyanthraquinone at 1621 cm^{-1} only.⁵⁶

Group frequencies will now be considered only briefly. Several excellent charts correlating a rather large number of atomic groups with the frequencies at which they are observed in absorption spectra—the so-called group frequency correlation charts^{3,7,24}—are available. The reader should see Chapter 6 for the excellent correlation chart developed by Norman Wright and his co-workers.

Hydrogenic Stretching Frequencies

Considering only the fundamental infrared from 5000 to 667 cm^{-1} , the highest frequencies observed are those involving hydrogenic str frequencies. Hydrogen, the lightest atom, can vibrate with the greatest vigor not only because of its mass but also because of its univalent character. Hydrogen-oxygen str vibrations occur from about 3700 to 3000 cm^{-1} with but few exceptions. "Free OH", i.e., hydroxyls not involved in hydrogen bonding, most frequently are observed in the 3700 to 3500 cm^{-1} range. They characteristically have narrower absorption bands as well as higher frequencies than the hydrogen-bonded hydroxyls (called "bonded" for short), which occur between about 3500 and 3100 cm^{-1} . More hydrogen-bonded hydroxyls are observed about 3333 cm^{-1} (3μ) than at any other frequency when one includes the majority of organic chemicals scanned in the infrared as liquids or solids.

It should be emphasized that occasionally both free and bonded OH will be found in one sample and their corresponding absorptions will both be observed in the infrared. This occurs most often when solutions of certain concentrations are involved. If one scans a $0.0001M$ solution of ethanol in CCl_4 solution, a narrow free OH str absorption is observed about 3650 and will be the only OH absorption observed between 3700 and 3100 cm^{-1} . If one scans ethanol in the liquid state vs air, a broad band of bonded OH str absorption is observed about 3350 cm^{-1} and will be the only OH absorption observed between 3700 and 3100 cm^{-1} . At concentrations intermediate between the dilute solution and as-is ethanol, one will observe both the free and bonded OH absorptions, the absorbances of which will

correspond to the concentrations of free and bonded OH present in the specific concentration of ethanol in CCl_4 scanned.

The exact frequency at which an OH absorption is observed is a measure of the strength of the hydrogen bonding extant in the molecule under study. The frequency variation observed in the OH absorption, when this molecule is scanned in solution in various solvents, gives a measure of the "solvent effect" or "medium effect" and helps elucidate the chemical structure of the molecule as it exists in solution.

It should be remembered that "group frequencies" are a useful technique based very largely on empirical observations, but also on theoretical assumptions, which normally represent a good approximation to the actual molecular facts. Like all rules of thumb, however, group frequencies are to be taken as the *probable* positions of characteristic infrared absorption bands. The author is not aware of any frequency range given in any spectra-structure correlation chart which is not "violated," however rarely, by some molecule. Most often these "violations" are more apparent than real, e.g., the 1621 cm^{-1} band of the carbonyls (the two carbonyl absorptions coincide because of the symmetry of the molecule) of 1,4-dihydroxy anthraquinone. In this instance, extremely strong hydrogen bonding of the oxygen of the carbonyls to the H of the adjacent hydroxyls, yielding a stable six-membered ring, endows the >C=O with enough single bond character to shift the normal aromatic ketone frequency from about 1680 to 1621 cm^{-1} .

The absence of a characteristic absorption in the range normally expected for any given atomic functional grouping is better evidence that such a grouping is missing from a molecule than the presence of such an absorption is evidence for the presence of the grouping. The explanation is simply that most observed absorptions have the possibility of arising from more than one functional grouping in a molecule. Or the observed absorption may be characteristic of the over-all structure of the molecule as a whole and not assignable to any specific molecular feature. Such bands arise from the coupling of several different vibrations.

N—H str frequencies are observed over about the same range as OH frequencies, since H is again so much lighter in mass than N, univalence is involved, and N and O are relatively close in atomic mass. Except for free N—H str, the observed absorption of an NH is normally narrower than for OH. This is a useful means of distinguishing NH and OH. When bonded OH is also present together with NH, however, the former often obscures the latter, preventing the N—H str region from being used to determine the presence or absence of the N—H grouping in an unknown. In such a situation, the N—H bending region from about 1650 to 1490

cm^{-1} can be used. More often than not, $\text{N}-\text{H}$ bending frequencies are observed in the close vicinity of 1540 cm^{-1} .

Owing to symmetrical and asymmetrical str vibrations, the $-\text{NH}_2$ grouping gives rise to two observed $\text{N}-\text{H}$ str frequencies usually about 125 to 150 cm^{-1} apart. Thus primary and secondary amines are readily distinguished. A secondary amide $\text{R}-\text{C}-\text{NH}-\text{R}$ will of course give rise



to only one $-\text{NH}-$ str vibration, and characterization as an amide can proceed if amide carbonyl at about 1665 cm^{-1} and a band about 1540 cm^{-1} are observed. The latter arises probably from a coupling among several vibrations, including the carbonyl, the $-\text{NH}$, perhaps the enol form, and others.

$\text{C}-\text{H}$ str frequencies usually are observed between about 3300 and 2700 cm^{-1} . In alkanes having both $-\text{CH}_2-$ and CH_3- groupings, a doublet is usually observed with a prism spectrophotometer near 2940 and 2850 cm^{-1} , while a triplet is seen on a grating spectrophotometer. The CH_3- grouping has symmetrical and asymmetrical $\text{C}-\text{H}$ str frequencies and so does the $-\text{CH}_2-$ grouping. These overlap, owing to their proximity to each other when observed on prism instruments. But three of the four absorptions can usually be observed on a commercial grating instrument. A helpful rule-of-thumb is that a $\text{C}-\text{H}$ absorption appearing above 3000 cm^{-1} arises from an "unsaturated $\text{>C}-\text{H}$," i.e., H attached to an aromatic ring C, an olefinic or acetylenic C, or a part of a highly halogenated grouping. By contrast, a $\text{C}-\text{H}$ absorption appearing below 3000 cm^{-1} arises from a "saturated $\text{>C}-\text{H}$," i.e., a H attached to a C having only single bonds

between it and the other atoms bonded to it. If one scans individual compounds, useful group str frequencies can be observed for various types of alkyl groupings such as ethyl, *n*-propyl, *n*-butyl, isopropyl and tertiary butyl, particularly under grating resolution. Usually, however, when such compounds are present in admixture with other components, these types of group str frequencies are of little use.

Triple Bond Stretching Frequencies

$-\text{C}\equiv\text{X}$ str frequencies usually are observed between about 2400 and 2050 cm^{-1} ; $-\text{C}\equiv\text{N}$ absorbs in the range 2400 to 2200 cm^{-1} . In many nitriles, one observes a single sharp absorption very near 2250 cm^{-1} . $-\text{C}\equiv\text{C}-$ gives rise to only a weak absorption ranging from 2280 to 2175 cm^{-1} and, when symmetrically positioned in a molecule, may not even be

observed. $\text{—C}\equiv\text{C—H}$, in addition to the hydrogenic str between 3300 and 3200 cm^{-1} , yields a medium strength absorption between 2175 and 2075 cm^{-1} . Isocyanide absorbs moderately between 2215 and 2070 cm^{-1} .

Double Bond Stretching Frequencies

C=O str frequencies are normally found between 1850 and 1640 cm^{-1} . The influence of neighboring atoms or groups attached to the carbonyl usually enables anhydrides, beta-lactam types, halocarbonyls, esters, acids, ketones, aldehydes, amides, etc., to be distinguished from the exact frequency location of the carbonyl absorption. Thus, e.g., ester carbonyls are normally observed between 1750 and 1710 cm^{-1} , acids between 1735 and 1660 cm^{-1} , ketones and aldehydes between 1740 and 1645 cm^{-1} , and amides between 1710 and 1630 cm^{-1} .

When ranges in wave numbers are given for the location of a group frequency, it means that absorptions for that specific grouping occur in various molecules anywhere within the range. More molecules containing that specific grouping will be found to absorb near the midpoint of that range than elsewhere. Thus, while ester carbonyl str covers 1750 to 1710 cm^{-1} , more ester carbonyls will absorb about 1730 cm^{-1} than at any other frequency location within that range. Similarly, acid carbonyls are most often found to absorb about 1710 cm^{-1} , ketones and aldehydes about 1690 cm^{-1} , and amides about 1665 cm^{-1} .

It cannot be overemphasized that the physical state in which a substance or sample is scanned is extremely important in determining the precise frequency range over which its functional groupings will show characteristic group frequencies. Thus monomeric propionic acid in the gaseous state yields a C=O str absorption at 1770 cm^{-1} ; in the liquid state the C=O str is observed at 1710 cm^{-1} ; the gaseous state dimer absorbs at 1754 cm^{-1} . Since carboxylic acids are normally dimeric but partially monomeric only in the vapor state, they are usually examined in the infrared in the solid or liquid state. While the frequency shift as between the liquid and solid states is normally less than between vapor and liquid, some shift will be observed. Accordingly, the spectroscopist should compare solution spectra vs solution spectra, solid vs solid, liquid vs liquid, etc. when identifying unknowns from known spectra or when drawing conclusions as to the origins of observed frequency changes in molecules of basically similar molecular structure.

C=N str frequencies occur from 1700 to 1580 cm^{-1} . Nonconjugated compounds containing the R—CH=N—R structure absorb in the range from 1675 to 1665 cm^{-1} . Imines, >C=NH , usually yield a moderate to

strong absorption between 1690 and 1630 cm^{-1} , while substituted imines containing the >C=N-C grouping normally absorb between 1670 and 1600 cm^{-1} .

In general, the C=N str frequency is difficult to identify. Its intensity can vary from weak to strong. In some conjugated ring compounds no C=N absorption is observed.⁶¹ For conjugated cyclic systems, C=N reacts with other double bonds and often cannot be assigned separately since, e.g., it often occurs with C=C groupings, which absorb in the same general region as C=N . It is extremely important that conclusions as to the presence of a C=N grouping in an unknown should never be drawn, except for unconjugated open chain and unconjugated cyclic systems, until one has examined a series of structurally similar materials of known structure in the same phase as the unknown.

C=C str frequencies absorb from 1700 to 1575 cm^{-1} . Most olefinic C=C 's are observed between 1680 and 1625 cm^{-1} when unconjugated, and usually about 30 cm^{-1} lower frequency when conjugated. It should be remembered that symmetrically situated C=C groupings, particularly in relatively large molecules, may show no, or at best a very weak, C=C absorption. It is most important that aromatic C=C str frequencies be distinguished in an unknown material, since their presence classifies at least one component and opens up the possibility of studying the very useful low-frequency (1000 to 600 cm^{-1}) "benzene substitution" absorptions. Further, the absence of aromatic C=C str normally eliminates all aromatics from consideration by the spectral interpreter. Aromatic C=C str frequencies occur from 1650 to 1550 cm^{-1} , and 1540 to 1450 cm^{-1} . A doublet is observed in the higher range, a singlet in the lower. While the weak intensity *para* disubstituted benzene absorption, occurring about 1625 cm^{-1} occasionally allows a specific assignment to be made on the basis of the aromatic C=C str, this is sometimes impossible, particularly if other types of aromatic components having different benzene substitutions are present simultaneously. In the usual situation, one is at most able to tell whether benzenoid components are or are not present from observing whether bands are or are not observed at about 1600 and 1500 cm^{-1} . The type of aromatic, how many of its ring carbons contain substituents other than H, and their precise location on the ring is usually determined from the aromatic C-H rocking frequencies occurring between about 1000 and 600 cm^{-1} . When only a single aromatic compound is scanned, or a mixture of two or three components having no functional group frequencies in the 2000 to 1667 cm^{-1} region, then this region may be successfully used to identify the number and position of carbons of the benzene ring which contain substituents other than hydrogen, as first discovered by Wright⁹⁸ *et al.* When

materials are scanned in the infrared, one or more of which yield a functional group absorption in the 2000 to 1667 cm^{-1} range, the resulting absorption(s) usually blots out the characteristic pattern in this region. In such instances, this region is not useful.

When condensed ring aromatics are under study by infrared, one must be cautious because the presence of large numbers of fused rings eventually causes the aromatic $\text{C}=\text{C}$ str to be found over broadened frequency ranges. The beginning spectroscopist considers naphthalene itself as an *ortho* disubstituted benzene for spectral interpretation purposes. And his first thought is borne out by experience. If one ring is unsubstituted, a strong band is observed in the range of 775 to 725 cm^{-1} , corresponding to the out-of-plane $\text{C}-\text{H}$ deformation vibrations (or "benzene substitution bands") characteristic of four adjacent ring hydrogen atoms, i.e., a characteristic *o*-disubstituted benzene absorption. Often it is also possible to identify the locations of the remaining free hydrogen vibrations on the substituted ring, corresponding to the particular type of tri- or tetrasubstituted aromatic molecule. When both rings in a naphthalene are substituted, however, the analogy with substituted benzenes often breaks down, and interpretive mistakes will be made if the spectroscopist considers such molecules merely as substituted benzenes. Here again, series of known molecules of closely related chemical structures must be scanned in the infrared, interpreted, and correlated, before even 95% confidence can be expected on interpretations of substances of unknown chemical structure.

It is not intended, in this brief summary of the background experience on which empirical infrared spectroscopy is based, to give in detail the probable positions of all group frequencies which various investigators have correlated.

Having briefly dealt with the str frequencies down through the double-bond region in order to give the reader a "feel" for group frequencies, the remaining single-bond frequencies will be covered in an even more brief manner. The reader should consult Bellamy, Colthup, and other correlation charts for more complete coverage of all group or characteristic frequencies.

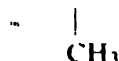
Single Bond Bending and Stretching Frequencies

$\text{N}-\text{H}$ bending frequencies are observed from 1650 to 1490 cm^{-1} . The presence of an absorption band near 1540 cm^{-1} immediately suggests the presence of an $-\text{NH}-$ grouping in the unknown, arising from a secondary amine, a monosubstituted amide, or an imine. While an RCOO^- grouping can absorb in this region, the 1425 cm^{-1} neighborhood can be examined to see whether or not the other characteristic pseudo-carbonyl absorption of an acid salt is present, to confirm or deny the presence of this functional

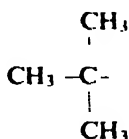
grouping. The nitro grouping also can show an absorption near 1540 cm^{-1} , but its greater intensity and the presence of an accompanying strong absorption in the 1300 to 1400 cm^{-1} region immediately distinguish this grouping. Similarly, no confusion with hydrochlorides normally results, because other higher-frequency regions serve to confirm or deny hydrochlorides. Imino carbonates will be recognized by the accompanying intensified absorption about 1660 cm^{-1} .

To determine whether an observed medium-to-weak intensity band arises from secondary amine, monosubstituted amide, or imine (assuming the other possibilities cited above have been eliminated), one seeks the presence or absence of a carbonyl near 1665 cm^{-1} . If present, monosubstituted amide is indicated. If absent, a strong band near 1655 cm^{-1} indicates an imine, while if neither an approximate 1665 or 1655 cm^{-1} band is observed, a secondary amine is suggested.

C—H bending frequencies occur between 1475 and 1300 cm^{-1} . The presence or absence of CH_3- and/or $- \text{CH}_2-$ groupings can be deduced from the presence or absence of a band near 1460 cm^{-1} . Similarly, the presence or absence of the CH_3-C grouping can often be assessed from the presence or absence of a band near 1375 cm^{-1} . The isopropyl and *t*-butyl structures can usually be identified from the relative intensities of their characteristic doublets in this region, provided the presence of other types of CH_3-C does not interfere. Molecules having the familiar CH_3-CH structure



show two bands of about equal intensity at 1360 and 1380 cm^{-1} . Those containing the



grouping show two bands at about 1360 and 1380 cm^{-1} , with the lower frequency one having appreciably greater intensity. A grouping comprising a methyl adjacent to a carbonyl, a methylene adjacent to a carbonyl or to a nitrile, and the $\text{>C}-\text{H}$ grouping (where only one hydrogen is attached

to a carbon exercising univalences only) can usually all be identified from the precise frequencies at which the C—H bending absorptions are observed.

O—H bending frequencies are observed from 1450 to 1200 cm^{-1} . Once the spectroscopist observes the presence of a potential hydroxyl grouping from the OH str near 3300 cm^{-1} , he consults the OH bending, C—O str,

and C—C str regions to determine the class of alcohol involved. Primary alcohols show their strongest band in this region, at about 1040 cm^{-1} , secondary alcohols near 1110 cm^{-1} , tertiary alcohols near 1160 cm^{-1} , and aromatic alcohols near 1230 cm^{-1} . Primary and secondary alcohols yield three characteristic absorptions in this whole region; tertiary and aromatic alcohols, two. It is important to realize that the extent of hydrogen bonding present in a specific alcohol, in the physical state in which it is scanned in the infrared, affects the precise frequency location of its absorptions in the 1300 to 1000 cm^{-1} range.

C—O str frequencies are observed from 1300 to 900 cm^{-1} and C—N str frequencies occur over the same range. C—C str frequencies absorb from 1200 to 800 cm^{-1} .

The reader has very probably noted that the frequency ranges over which single-bond str frequencies are observed is greater than that for double-bond str, which latter is greater than for triple-bond str. In general, the forces holding triply bonded atoms together are about 1.5 times greater than for doubly bonded atoms, which in turn are about twice those for singly bonded atoms. Accordingly, interatomic distances are shorter for a triple bond than for a double-bond, which in turn is shorter than for a single bond. Hence, nearest-neighbor atomic groupings have relatively little effect on the frequency location of a triple bond, somewhat more effect on the frequency location of a double bond, and a large effect on the frequency location of a single bond. The range of frequencies over which single-bond str absorptions are observed is wide, that for double-bond str absorptions is narrower, and that for triple-bond str absorptions is quite narrow. By the same token, absorptions of multiple bonds are most easily identified in unknowns, while single-bond linkages, such as carbon-carbon, are observed over such a wide range of frequencies that they are usually very difficult to identify.

Rocking Frequencies

C—H rocking frequencies are observed from 900 to 600 cm^{-1} ; N—H rocking frequencies are observed from 900 to 700 cm^{-1} .

Probably the C—H rocking mode of greatest use is that of the $-\text{CH}_2-$ grouping, which is observed near 725 cm^{-1} , arising from an open chain of four or more adjacent methylene groups. In hydrocarbons the range for this band is about 760 to 720 cm^{-1} . No band is observed in this range for the cycloparaffins until cycloheptane, which shows a 734 cm^{-1} absorption. Cyclooctane has a band at 766 cm^{-1} .

A convenient technique for deciding whether a band observed near 725 cm^{-1} arises from this $-\text{CH}_2-$ rocking mode is to examine spectra in different states. This band is always a doublet below the transition point

and in the solid state, but a single absorption in the liquid state and in solution. Since the doubling of this band arises from interactions between neighboring molecules in the crystalline state, studies of the relative intensities of these bands offer a convenient method for determination of the crystalline/amorphous ratio.

The author has observed the presence of a 725 cm^{-1} band in several molecules of known structure which contained the grouping

$\begin{array}{c} | \\ -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}- \end{array}$ and similar structures closely related to $-(\text{CH}_2)_{4 \text{ or more}}$ but not precisely this latter group. Therefore, caution needs to be exercised in assigning an observed band near 725 cm^{-1} in an unknown. The absence of a band here, of course, is excellent evidence that no open chain $-(\text{CH}_2)_{4 \text{ or more}}$ structural unit is present.

Miscellaneous Group Frequencies

The nitro group shows two very strong absorptions with the conjugated nitro absorbing at somewhat higher frequency for both. In the unconjugated case, the bands are observed near 1340 and 1540 cm^{-1} ; for a conjugated nitro, the bands are observed near 1370 and 1560 cm^{-1} .

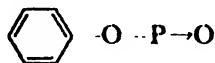
Covalent nitrite groups ($\text{R}-\text{O}-\text{NO}$) absorb in the 1675 – 1590 cm^{-1} range, while the nitroso structural unit ($\text{R}-\text{NO}$) is observed between 1420 and 1320 cm^{-1} .

Both sulfonic acid ($\text{R}-\text{SO}_3\text{H}$) and ionic sulfonate yield bands near 1200 and 1050 cm^{-1} , the former a stronger absorption. The sulfonic acid will, in addition, show a medium strength hydroxyl band in the 3500 to 3100 cm^{-1} range.

Covalent sulfonate ($\text{R}-\text{O}-\text{SO}_2-\text{R}$) absorption is strong near 1370 and 1175 cm^{-1} , while covalent sulfate ($\text{R}-\text{O}-\text{SO}_2-\text{O}-\text{R}$) absorbs strongly near 1400 and 1190 cm^{-1} .

Sulfonamides ($\text{R}-\text{SO}_2-\text{NH}_2$) show strong bands near 1340 and 1160 cm^{-1} ; sulfones ($\text{R}-\text{SO}_2-\text{R}$) near 1320 and 1140 cm^{-1} ; and sulfoxides near 1050 cm^{-1} .

Covalent phosphate [$(\text{R}-\text{O})_3\text{P}\rightarrow\text{O}$] of type $-\text{CH}_2-\text{O}-\text{P}\rightarrow\text{O}$ absorbs strongly near 1275 and 980 cm^{-1} , and type



absorbs strongly near 1275 and 1220 cm^{-1} .

The $\text{Si}-\text{CH}_3$ grouping yields a strong sharp absorption over the narrow 1259 to 1250 cm^{-1} range, and the number of methyls attached to the silicon can usually be determined by examining bands observed in the 840 to 800 cm^{-1} region. $\text{Si}(\text{CH}_3)_4$ absorbs near 1259 cm^{-1} and near 800 cm^{-1} ;

$\text{Si}(\text{CH}_3)_2$ near 1259 cm^{-1} and in the 814 to 800 cm^{-1} range; $\text{Si}(\text{CH}_3)_3$ near 1250 , 841 , and $756\text{--}754\text{ cm}^{-1}$.

Since Si-atom linkages absorb about five times more intensely than the bands from corresponding C-atom linkages, the spectroscopist normally has little difficulty in characterizing silicon derivatives. Therefore, infrared is widely useful in developing, identifying, and controlling silicone oils, polymers, etc.

The Si--O-Si grouping can usually be identified from infrared spectra, and determination can be made of its origin, i.e., whether in an open chain structure or cyclic. If the latter, the precise location of the frequency can reveal the presence of a trimer, tetramer or even higher ring. Open chain Si--O--Si absorbs in the 1090 to 1020 cm^{-1} region; cyclic trimers, 1020 to 1010 cm^{-1} ; tetramers, 1090 to 1080 cm^{-1} ; larger rings, from 1080 to 1050 cm^{-1} . All the absorptions given are very strong ones.

Very strong characteristic absorptions are also observed for the Si-phenyl, Si--O--C, and Si--H groupings. Owing to the existence of polymorphism, of hydrogen bonding in certain silicones, and the very narrow spectral range of several Si-atom absorptions, it is most satisfactory, where possible, to carry out infrared work in solution when studying silicon-containing materials.

The CF_2 and CF_3 groupings absorb between 1350 and 1200 cm^{-1} ; $\text{>C}=\text{F}$ (unsaturated) between 1225 and 1090 cm^{-1} ; and $\text{>C}-\text{F}$ (saturated) between 1110 and 1000 cm^{-1} . All of these bands are very strong. C--F absorption in general is exceptionally strong, owing to the very great electronegativity of fluorine.

Characteristic Frequencies of Inorganic Ions

As previously mentioned, monatomic atoms and ions do not usually absorb infrared. All polyatomic cations and anions show absorption, however. Therefore, when an inorganic compound or complex contains either a polyatomic anion or cation or both, infrared radiation will be absorbed. Thus borate, carbonate, nitrate, sulfate, ammonium, phosphate, molybdate, cyanide, ferro- and ferricyanide, etc., show characteristic infrared absorption bands. Sulfates, e.g., absorb near 1110 cm^{-1} ; nitrates, sharply at medium intensity near 830 cm^{-1} and strongly near 1770 cm^{-1} ; the ammonium ion, strongly near 1390 cm^{-1} and moderately near 3100 cm^{-1} .

The most widely useful spectra-structure correlation chart for the characteristic frequencies of inorganic ions is still that of Miller and Wilkins.⁶⁸ The reader is referred to Chapter 17 for applications of infrared spectroscopy to inorganics. Bellamy⁷ presents an excellent critical review of the data on which infrared spectra-structure correlations are based.

QUALITATIVE ANALYSIS

The basis of qualitative analysis by infrared spectroscopy is that no two substances which absorb infrared radiation absorb it at the same frequencies to the same extent. Thus, an infrared absorption spectrum is a "fingerprint" of a substance as unique as the fingerprint of a human and as useful in differentiating one molecule from another as human "prints" are in differentiating one individual from another. Moreover, the spectrum of a mixture of components, barring those relatively few cases where hydrogen bonding or chemical reaction takes place, is simply the sum or superposition of the spectra of the individual components comprising the mixture. This fact is in rather sharp contrast to UV and VS (visual) spectroscopy where pH and other effects often negate the additivity. Infrared is the most widely used technique for identification of unknown substances and mixtures.

After the spectroscopist has become familiar with the spectrum of dimethyl-*o*-phthalate plasticizer, for example, he will probably recognize it in the spectrum of an unknown single liquid substance scanned at a later date. And if memory is in doubt, he can withdraw the known spectrum from his files and confirm or deny this plasticizer's presence. Should he observe an ester absorption in a mixture spectrum, the characteristic *o*-phthalate aromatic C=C str doublet at about 1600 and 1580 cm^{-1} , and the telltale *o*-phthalate "benzene substitution" absorptions at 705 and 745 cm^{-1} , he can compare against his file of known *o*-phthalate spectra to learn which such ester is present: After identifying the exact *o*-phthalate present, he then can turn to interpreting and identifying those absorption bands in the spectrum which are still unaccounted for.

The infrared spectrum of a substance yields a graph of the mechanics of the molecule in motion. In contrast to single-valued data like melting points, boiling points, etc., the spectrum presents some 30 to 50 physical values which characterize the substance. Thus, the great value and widespread use of infrared spectroscopy as a means to identify substances and elucidate molecular structure.

Infrared analyses are rapid and require only a very small amount of sample, and the procedure is not destructive of the sample. For many types of projects in the chemical, biological and pharmaceutical fields, these latter two attributes are a *sine qua non*, because isolation procedures and synthetic procedures often result in only micrograms or milligrams of final product. In a number of infrared labs today, useful spectra are obtained on materials in the 10 to 100 μg range (see Chapter 16).

The criterion for qualitative identification of an unknown single substance or mixture of substances is that the spectrum of the unknown must match

precisely the spectrum of the known(s) in both frequency location of absorption bands and intensities. In short, the known and the unknown spectra are able to be superimposed and found identical. In the absence of a known spectrum which matches an unknown, the spectroscopist can only predict or suggest possible structures. He can never be certain, and should turn to chemical or other physical procedures to complete the identification. Or, he should have his "proposed structure(s)" synthesized and then carry out the infrared spectral superposition test.

Qualitative infrared analyses can be carried out on materials in any physical state - gas, liquid, solid, solution, or in-between states. Normally no chemical action is produced by the infrared radiation penetrating a material other than a heating effect which is usually minor. All organic materials and all inorganics having polyatomic cations and/or polyatomic anions are amenable to infrared analysis.

Since the vibrational infrared spectrum in the 5000 to 400 cm^{-1} (2 to 25μ) region can be classified approximately into those frequencies which are characteristic of small groups of atoms within a molecule (group frequencies) and those which are characteristic of the molecule as a whole, other qualitative problems in addition to identification can be successfully attacked. Such qualitative information as the following can be obtained from proper study of the spectra of an unknown substance or mixture:

- (1) Examination of simple mixtures may be made to learn whether or not any chemical reaction has taken place upon admixture. If the spectrum of the mixture is not the simple sum of the spectra of the individual components, then chemical reaction has occurred. And often what reaction has occurred can be discovered.

- (2) If a substance is known to be a single chemical and is thought to be one of several possible known chemicals whose infrared spectra have been or can be scanned, spectral comparisons can readily show which of the presumed structures is the correct one.

- (3) If a newly synthesized or isolated material is known or can be shown to be a single chemical substance, then its infrared spectrum, upon interpretation of the functional groupings present and other structural features, can offer valuable aid to the determination of the structure, and in some cases can determine the structure by itself. Proof, of course, can come only after the new substance has been prepared and its spectrum shown to be identical to the new material.

- (4) If the purity of a single substance needs to be assayed, spectral comparison against the spectrum of the substance of known purity can often lead to identification of the impurities present, and with suitable quantitative procedure lead to a determination of the impurities. Normally nonpolar impurities will be difficult to detect at less than 1% concentration

at normal scanning thicknesses, but by judicious choice of analytical frequencies and large sample thicknesses, the limiting sensitivity can be materially improved upon. Polar impurities can normally be detected at much lower limits and sometimes at the 0.01% level and better. The sharpness of absorption bands can sometimes -- not, of course, when all absorptions are broad -- be successfully used to judge purity. Much more can be done in this direction than has currently been revealed in the literature.

(5) If an unknown is a mixture of chemical components, systematic interpretation of its spectra with respect to functional groups present and absent, as well as other over-all molecular structure information revealed, can lead to successful comparisons against known spectra suggested from the interpretations, revealing the identity of the components of the mixture together with a rough estimate of their percentages. This latter semi-quantitative result is obtained through comparison of relative intensities versus known material relative intensities.

(6) All isomers except optical enantiomorphs can be distinguished by means of their infrared spectra. The spectroscopist will find this technique useful in differentiating *cis-trans* and keto-enol isomers, e.g.

(7) Polymorphic forms of both organics and inorganics can be differentiated through use of infrared. The infrared technique is not limited, as is the x-ray technique, by the presence of amorphous materials or by amorphous regions in polymers, but in fact can give useful results in crystallinity studies (see Chapter 8). If two materials known to be single chemical substances yield different infrared spectra in the solid state, yet identical spectra in the solution state, then the two are polymorphic forms of the same chemical material.

(8) The study of the kinetics and mechanism of a chemical reaction is sometimes possible by infrared, particularly for those reactions which are not instantaneous, i.e., many organic reactions and a few inorganic ones.

(9) The determination of the orientation of polymers, fibers, and the like can successfully be attacked by infrared, normally most profitably through the use of polarized infrared radiation.

(10) Adsorption of molecules on surfaces can be tackled and useful information can be obtained in the field of catalysts, protective coatings, and the like.

(11) The synthetic organic chemist finds infrared extremely useful in quickly deciding whether a given reaction has taken place, whether a reaction has gone to completion, what the side-reaction products are, whether a desired functional grouping has been formed, etc.

(12) The infrared spectrum of a new chemical, synthesized or isolated, is the best proof obtainable, to present with a patent application, that a new material has truly been discovered.

(13) The usefulness of infrared in qualitative analysis is limited primarily only by the experience and the ingenuity of the spectroscopist.

To successfully uncover the qualitative information described above, a table of group frequencies or a spectra-structure correlation chart is essential. These group frequency values are readily transferable from one spectroscopic laboratory to another, but transference of catalogs of infrared absorption spectra are usually helpful though not entirely satisfactory. All too often one has scanned the spectrum of a solid as a mineral oil mull, believes he knows approximately what this unknown is, and then finds to his consternation that his purchased catalog(s) of spectra gives the likely known only as a scan in CCl_4 and CS_2 solution. Moreover, any laboratory carrying out serious infrared spectroscopy soon finds its own particular problems call for spectra not previously published. It is wise, therefore, for each laboratory to set up its own collection of spectra. Published collections of others fill gaps in one's own collection but are often poor substitutes for a collection on one's own instrumentation.

In making comparisons of spectra of unknowns vs knowns, the spectroscopist should remember that to be valid the comparisons must be made on spectra scanned under comparable conditions in the same phase. Infrared spectra of the same substance or material scanned as mineral oil mulls and KBr pellets are sometimes different. In addition to potential halide exchange, polymorphic transitions as well as other effects arising from heat and pressure (see Chapter 14) can make a KBr spectrum look like a different material compared to the spectrum of this same sample scanned as a Nujol mull. And the spectrum of a melt between NaCl plates, cooled to room temperature and scanned, quite often is different from this same material scanned as a Nujol mull. The spectrum of the solution of a substance in a highly polar solvent will sometimes show spectral differences as compared to its scan in a nonpolar solvent. As every experienced spectroscopist learns, an improperly prepared mull or halide pellet can produce false and misleading results. Potts (Chapter 6) presents a useful discussion on the proper preparation of mulls. For suggestions on sample preparation for infrared, the reader is referred to Chapter 4.

Just as there are spectra-structure correlations for functional groupings and other molecular features of organic substances, so also are there charts of the characteristic frequencies for ions (see Chapter 17). While all organics absorb infrared, atoms and monatomic ions in general do not. Neither do diatomic molecules possessing only one kind of atom owing to lack of dipole moment change during vibration. All inorganics containing polyatomic cations and/or anions, however, do absorb infrared radiation. It is primarily the covalent bonding existing in a polyatomic cation, such as NH_4^+ , or polyatomic anions, such as sulfate, carbonate, borate, and the

like, which give rise to infrared absorption. Therefore, qualitative analysis on inorganics can be carried out just as for organics. In general, inorganic spectra are featured by fewer and broader absorption bands than organic spectra.

Despite several intensive studies of infrared spectra of inorganics over the last fifteen years, the exploitation of infrared for inorganic materials is still in its infancy and deserves much more attention. For applications of infrared to inorganics, see Chapter 17.

QUANTITATIVE ANALYSIS

Mixtures of organic materials soluble in appropriate solvents and certain mixtures of both organic and inorganic materials possessing rather high water solubility can be quantitatively analyzed by infrared. At some loss in accuracy, melt methods can be handled quantitatively, and gas analyses can be carried out provided proper standard mixtures are chosen to eliminate pressure-broadening effects. For insoluble materials, a number of halide disk methods (such as KBr) have been published with accuracy reasonable for many commercial purposes. Usually mull methods, even with the use of internal standards, are rather unsatisfactory.

Infrared quantitative analyses are particularly valuable for the determination of chemical substances which are closely related structurally, such as geometrical isomers. The ability to use small samples, to be able to recover the samples intact for other measurements, and the speed of carrying out the work, make quantitative infrared analysis one of the most valuable applications of infrared techniques. Moreover, a permanent, readily filed record is obtained, which can conveniently be checked or examined at any future time.

Quantitative analysis is carried out by comparing the absorption of a selected infrared band shown by a component in a mixture to be analyzed with the absorption shown by this same band from a pure material under similar conditions at known concentration. The quantitative function used to measure the absorption strength is absorbance, A . From Equation (1-6), $A = abc$

where

a = absorptivity which almost always is cancelled out but can be expressed in appropriate units

b = path length in cm

c = conc. in g/liter.

Since A also = $\log I/T$, spectrometer graphs for quantitative analysis are printed with a logarithmic absorbance scale for the ordinate to facilitate measurement of A differences. Absorbance measurements can also be made

from % T graphs through use of a transparent ruler laid out on the absorbance scale.

Because A is directly proportional to c and absorptivity is the proportionality factor, absorbances are additive. Furthermore, absorptivities of components being determined and these same absorptivities in the known standards cancel out. Likewise for cell thickness, b , since one preferably uses the identical cell for scanning both standard and unknowns. Thus, quantitative infrared analysis resolves into measuring A to determine c . The additivity of A 's makes multicomponent analyses possible.

The reason the same infrared cell is used for knowns and unknowns is that to obtain quantitative accuracy, cell path lengths cannot vary by as much as 1%. And the usual infrared cell window material, such as NaCl, e.g., does not have the same thickness the second time it is filled as it does the first, owing to the very low but still finite solubility of water in most organic solvents. And NaCl is readily fogged and eroded by low percentages of moisture.

The vast majority of quantitative infrared work is carried out in solution because cell thickness is best and most readily controlled using solutions. Molecular interaction effects are also reduced in the solution phase. While some analyses can be carried out on liquid mixtures sans solvent, normally concentrations of one or more components will yield A 's too high to measure accurately without dilution in solvent.

The substance to be analyzed must possess a reasonably intense absorption not greatly interfered with by absorptions of other components present. In solution work, this, of course, includes the solvent which ideally should show as little infrared absorption of its own as possible. The best infrared analytical solvents, such as CCl_4 or CS_2 are obviously ones showing transmission of infrared radiation over as wide a wavelength range as possible. Such good "infrared window" solvents show limited solubility particularly for polar solutes. Any organic solvent which does not attack the cell material being used, in which the solute has adequate solubility, and which has windows at the required infrared bands, can be used. Even regions of partial solvent absorption can be used by scanning differentially vs the pure solvent in the reference beam of a double-beam infrared spectrophotometer.

The absorption bands at which components are to be determined are called "analytical wavelengths." The first step in quantitative analysis is to select a suitable solvent, using the criteria given above. The second step is to select an analytical λ suitable for determining each component. This is done by scanning each pure known component in the solvent selected, over a wavelength range covering all analytical wavelengths concerned. Comparison of these spectra will reveal which band or bands best

meet the criteria for analytical λ selection. Scanning of the pure knowns will suggest the best solvent concentration to use and the most appropriate thickness of the fixed-thickness-cell. Concentration and cell thickness are selected with the goal of optimizing accuracy and precision. Owing to the logarithmic nature of the A ordinate, greatest accuracy in A measurement can be made at $A = 0.432$ (37% T) for a one component analysis. In general, for multicomponent analyses, A should remain within the range of 0.600 to 0.300 (25.1 to 50.0% T) for reasonable accuracy.

Few quantitative analyses are performed with more than five components; most involve but two or three, although analyses reported in the literature run to as high as ten components. Clearly, the number of components which can be handled depends upon how willingly each component to be analyzed yields strong absorptions not largely interfered with by absorptions of any other component or the solvent. In some cases, the spectroscopist will have difficulty finding unique analytical λ 's for three components; in others, he will readily find analytical λ 's for five. How chemically dissimilar the components are will suggest whether a given multicomponent analysis is possible (when more than three components are involved). In any case, the analysis should be attempted, if the worth of a successful method warrants the investigation.

Cell-In-Cell-Out Method

Absorbance measurements on quantitative infrared scans are made usually by the "cell-in-cell-out" or the "base-line" method. The former is presently the principal use to which single-beam spectrometers are put. The instrument is set at the fixed analytical λ using a fixed slit width normally, quantitative slit widths are approximately double those used for qualitative spectral scanning. Briefly, the procedure is as follows:

(1) The known solution containing the unknown substance U being determined in known concentration in the selected solvent and fixed cell thickness has its % T measured at the analytical λ , the absorption maximum, i.e., transmission minimum. The resulting value is I , the transmitted intensity.

(2) Measurement at the same λ is made with pure solvent filling the same cell. The resulting I_0 is the per cent transmitted by the cell and solvent, when no absorbing molecules of interest are present.

(3) Measurement at the same λ is made by placing a selected material in the beam known to be opaque at the anal. λ , but transparent at shorter wavelengths. The resulting 0% T is the true zero, free of scattered light.

The A of unknown U is then measured, using an absorbance ruler (or converting the % T 's to A 's from a conversion table). The ∞ on the

ruler is placed on the true zero and subtraction of the I_0 from I value made, to yield the A of U.

Steps 1, 2, and 3 above are repeated using the "reference (standard) solution," a known c solution of pure U in the same solvent and cell, and the A determined as for the unknown.

The per cent U in the unknown mixture is now calculated.

For the unknown:

$$A_{U, \text{unk}} = a_U b_{\text{unk}} c_{U, \text{unk}} \quad (2-1)$$

for the known:

$$A_{U, \text{ref}} = a_U b_{\text{ref}} c_{U, \text{ref}} \quad (2-2)$$

Since the a 's are constant and the same cell is used for both unknown and reference solutions, the b 's also cancel.

Hence,

$$\frac{A_{U, \text{unk}}}{A_{U, \text{ref}}} = \frac{c_{U, \text{unk}}}{c_{U, \text{ref}}} \quad (2-3)$$

Using the convenient weight per volume per cent system, then

$$c_{\% \text{ U by weight}} = \frac{A_{U, \text{unk}}}{A_{U, \text{ref}}} \cdot \frac{c_{U, \text{ref}}}{c_{U, \text{ref}}} \quad (2-4)$$

where $c_{U, \text{ref}}$ = weight per volume per cent, the weight of sample of unknown composition per volume of its solution, i.e.

$$c_{U, \text{ref}} = \frac{c_{U, \text{unk}}}{c_{\% \text{ U by weight}}} \quad (2-5)$$

Base-line Method

While the cell-in-cell-out method is simple, precise, and time-saving, for many analyses it yields errors owing to inability to yield a correct value of I_0 , the per cent transmitted by the cell and solvent when no absorbing molecules of interest are present. The "base-line" method minimizes such errors by yielding a better approximation to the true I_0 . Most often a tangent is drawn between absorption minima contiguous to the absorption maximum (the analytical λ) on either λ side of it as illustrated in Figure 6-8 (Chapter 6). The A is then obtained by subtracting the A at the absorption maximum from the A at the base line.

In the "base-line" procedure, the spectrum is scanned over the analytical λ 's for each component being determined, using either a double-beam spectrophotometer or a single-beam instrument with slits programmed to give constant energy. In essence, the "base-line" represents the closest practical approximation to the true absorbance of the absorption band at an analytical λ in quantitative infrared analysis, compensating for non-

specific but finite generalized absorption contributed by other components and other factors such as scattering by dispersed solids in a "solution" at any given analytical λ .

The important factors to keep in mind when using the base-line technique are:

(1) The tangent-line construction is the best, since it is more reproducible than French-curve or free-hand constructions connecting the minima on either wavelength side of the analytical λ .

(2) The known mixture, prepared as a reference standard, should contain a concentration of each of the known components being determined as close as possible to their respective concentrations in the unknown composition being analyzed.

(3) Accuracy will be highest when the base-line is drawn at low absorbance values and as near horizontal as possible.

(4) Always scan the complete spectrum of an unknown quantitative composition even though the components being determined require only a scan of 2 or 3 μ covering two analytical λ 's. Such a complete scan can save much time by occasionally revealing the unknown is quite different from what one had been assuming all along.

In general, quantitative infrared analyses, with proper care and precautions, can yield accuracies of about $\pm 1\%$ of the amount present of the substance being determined. Very careful weighing, voluming, and manipulative technique are required to obtain such accuracy, as well as a properly functioning infrared instrument, careful measurement of absorbance values, etc.

Working-Curves

Whenever the relation $A = abc$ is made the basis of a quantitative infrared analysis, the assumption is made that Beer's law is obeyed, namely, that a plot of absorbance vs concentration yields a straight line passing through the coordinate origin. Accordingly, before the spectroscopist can put any faith in a quantitative analysis by infrared, he must check to see whether or not Beer's law is obeyed, by scanning at least three knowns covering the range of concentrations over which he intends to analyze his unknowns, and examine the A vs c plot. If a straight line results, he can use the simple $A = \epsilon bc$ relation. If not, he must prepare a "working-curve," scanning enough known concentrations to yield an accurate working-curve of A vs c . Subsequently, he uses the working-curve to read off c values from measured A 's. The working-curve approach is normally only warranted for analytical control or in special investigations requiring a relatively large number of similar quantitative determinations to be made.

The Elements of the Beer-Lambert Law

The absorptivity, a , in the equation $A = abc$ is an exact value only for a monochromatic beam of radiation. All spectrophotometers, however, have finite spectral slit widths passing several different wavelengths. Thus, only an average a is possible, and this average a can be exact at only one wavelength. In a Beer's Law plot of A vs c , the linearity of the plot is a function of the slit width; the narrower the slit, the more linear the plot, since narrower slits approach monochromatic radiation more closely. Accordingly, analytical slit widths should be as narrow as possible, consistent with proper signal-to-noise ratio to insure the best accuracy. In general, a Beer's Law plot should deviate from linearity by 1% or less over the concentration range concerned.

The fact that absorptivity is a function of spectral slit width is the key to why accurate A data and hence quantitative analyses can not be transferred readily from one infrared spectrophotometer to another, even of identical make and model number. Despite the best efforts of infrared instrument manufacturers, they have so far not been able to reproduce exactly the width and shape of the spectral slit from one instrument to the next on the same electromechanical optical assembly-line. Thus, transference of quantitative data among instruments still remains a challenge to the instrument makers. The desirable consequence of greatly enhancing the wider use of quantitative infrared analysis would result from the exact transference of data. The advent of grating spectrophotometers of wide wavelength-range resolution of 1 cm^{-1} offers hope in the direction of transferability of infrared data from instrument to instrument. Very much work needs to be done in this direction. Furthermore, while published values of " a " and percent T vs λ plots can be used to suggest the possibilities for an analysis, each spectroscopist must still determine his own values on his own instrument, including limits of error involved.

The smaller the intermolecular forces between the components of a mixture undergoing quantitative determination, the closer the approach to linearity of a Beer's Law plot. This is because the absorptivity values are for one specific chemical species at one exact wavelength. Diminution or increase of this specific species by intermolecular reaction obviously decreases or increases the value of " a ." Straight-line Beer's Law plots, then, will be most likely with nonpolar solute: in nonpolar solvents. For polar materials, as dilute solutions as can be handled in the least polar adequate solvents will give the best likelihood of linear plots.

As indicated earlier, deviations from Beer's Law are greatest at high concentrations. Thus minor components often obey the law more closely, yielding more accurate analyses. It is sometimes simpler and more accurate,

therefore, to analyze for the minor components only, and determine the major component by difference.

In any given mixture, one potential analytical wavelength may follow Beer's Law more closely than another.⁵⁷ Thus the infrared analyst should try out the second strongest potential analytical λ for a component, if the strongest potential analytical λ is found to deviate from Beer's Law. Analytical wavelengths are normally selected for each component in turn, using as unique and as strong an absorption as possible, i.e., the analytical λ shows very strong absorption for the given component, while the remaining components show as little absorption at this λ as possible. Occasionally λ 's may be found for which all the components but one possess nearly identical absorptivities. Consequently, one has essentially a two component mixture at this λ . Here is a location preferable to some other where the difference in a 's is greater because of the simplicity and higher accuracy obtainable.

Multicomponent Analysis

Whenever it is possible to find an analytical λ for each component in a mixture, where none of the other components show any absorption, then the simple $A = abc$ relation can be employed for determining all components in turn. It frequently occurs, however, that one or more components in a mixture will yield no absorption band which is free of significant absorption by one or more of the other components present. In this circumstance the "additivity of absorbances" feature of Beer's Law is taken advantage of. The absorbance of a mixture of components at given wavelength λ is equal to the sum of the absorbances of all the components at that λ . Taking A_T as the total A at wavelength λ , then letting superscripts 1, 2, 3, etc. refer to the different components, A_T is found by

$$A_T = a^1c^1b + a^2c^2b + a^3c^3b + \cdots \text{etc.} \quad (2-6)$$

For a three component mixture, designating the analytical wavelengths by subscripts 1, 2, and 3, the A 's at the three λ 's can be written

$$\begin{aligned} A_1 &= a_1^1c^1b & a_1^2c^2b & a_1^3c^3b \\ A_2 &= a_2^1c^1b & a_2^2c^2b & a_2^3c^3b \\ A_3 &= a_3^1c^1b & a_3^2c^2b & a_3^3c^3b \end{aligned} \quad (2-7)$$

and

$$A_T = A_1 + A_2 + A_3$$

Normally the same cell is used during an analysis, so b is not measured explicitly but rather incorporated into the determination of " a ." Thus, writing the above equations, using a new " a " as including the " ab 's":

$$\begin{aligned}
 A_1 &= a_1^1 c^1 & a_1^2 c^2 & a_1^3 c^3 \\
 A_2 &= a_2^1 c^1 & a_2^2 c^2 & a_2^3 c^3 \\
 A_3 &= a_3^1 c^1 & a_3^2 c^2 & a_3^3 c^3
 \end{aligned}
 \tag{2-8}$$

Obtaining the values for the a 's in the above expressions using pure materials and for the A 's of the mixture permits a calculation of the desired concentrations " c ." If many analyses of this three component system, e.g., are to be carried out, simplification results by transposing the above equations by reciprocal (or inverse) matrix methods, or by computers, to the following form:

$$\begin{aligned}
 c^1 &= a_1^1 A_1 & a_1^2 A_2 & a_1^3 A_3 \\
 c^2 &= a_2^1 A_1 & a_2^2 A_2 & a_2^3 A_3 \\
 c^3 &= a_3^1 A_1 & a_3^2 A_2 & a_3^3 A_3
 \end{aligned}
 \tag{2-9}$$

where c^1 , c^2 , and c^3 are the concentrations desired.

The applicability of the described procedure to a given analysis depends upon the extent to which the Beer-Lambert Law is obeyed. If experimental determination of the A vs c plots of the components in the mixture form straight lines, the procedure can be followed directly. The more such plots deviate from linearity, the more complex become the calculations to correct for the non-linearity. Time spent in finding experimental conditions which satisfy Beer's Law, whenever possible, is justified by the consequent ease of calculation, if the investigation is successful. The required calculations are greatly simplified through use of computers (see Chapter 18).

When Equations 2-8 do not hold with the accuracy required, the methods of "successive approximations" or of "applied corrections" are used.^{31,40} When Beer's Law is badly violated, empirical working curves of A vs c for each component being determined must be set up with several A measurements of each pure reference material made over a wide concentration range.

As a general rule of thumb to assess when a multicomponent quantitative analysis by infrared will not be feasible whenever the only available potential analytical λ 's are very broad, then the overlap of absorptions of the various components at each such potential analytical λ will be so great that sufficient accuracy will not be provided by an infrared procedure. The spectroscopist should always bear in mind that infrared is not the only quantitative analytical technique available and it should be attempted and used only when its advantages outweigh those of alternative quantitative analytical procedures.

Specialized Quantitative Analytical Techniques

When a quantitative infrared procedure is indicated but search and trial-and-error have not produced a suitable solvent, techniques other than

solution procedures must be resorted to. Such procedures include ratio methods, pressed disk techniques, use of internal standards, melts, and films. While a few quantitative methods have been developed using mulls, in general mulls are unsatisfactory for quantitative work. To duplicate the degree of dispersion, the amount of scattered light, the film thickness, and the homogeneity of the mull is normally not possible. Both accuracy and precision suffer.

Ratio Methods. The ratio method can be used for films, pressed disks, or pressed films. The films can be cast from solution in solvents or solvent mixtures, which may be the only liquids which will dissolve the material, but which are unsuitable solvents for quantitative analysis in solution. Or a film of liquid at capillary thickness may be used. In general, the ratio method is used when one is unable to measure with accuracy the thickness of the sample to be scanned in the infrared. Quantitative determination is usually made on a relative rather than an absolute basis, through use of absorbance ratios. If the sum of the concentrations of the components being determined is known and equals 100%, then each component can be determined exactly on an absolute basis. Ratio methods most often are used for two component mixtures, occasionally three, but seldom more, because of the difficulty in obtaining reference standards of known composition and the time required to set up working curves of absorbance ratios vs concentration ratios for a broad composition range. It is necessary, of course, to be able to prepare the material which is to be scanned in a uniform homogeneous "film," at least over the area which the infrared beam irradiates.

Presume one desires to determine the quantitative composition of a material which is known to contain only components A and B. If the spectroscopist can find an absorption for A uninterfered with by B and vice-versa, which obey the Beer-Lambert law, then

$$\begin{aligned} A_A &= a_A b c_A \\ A_B &= a_B b c_B \end{aligned} \quad (2-10)$$

Since we are scanning one and the same "film," the path length "b" is the same for each of the two absorptions as indicated in the above equation. Letting R = the absorbance ratio, then,

$$R = \frac{A_A}{A_B} = \frac{a_A c_A}{a_B c_B} = m \frac{c_A}{c_B} \quad (2-11)$$

where m is the slope of the line when Beer's law is obeyed or the slope of the curve when Beer's law is violated.

From "films" of known composition of A and B, but of indeterminate path length, spectra are scanned, absorbance measurements made on the same bands by the same measurement technique, and absorbance ratios obtained therefrom. Knowing the "c's" of A and B, "m" is then readily calculated and thereafter the concentration ratio in the unknown. Since $c_A + c_B = 1$,

$$c_A = \frac{R}{m + R} \quad \text{and} \quad c_B = \frac{R}{m + R} \quad (2-12)$$

Thus, the exact concentrations of A and B in the unknown are quantitatively determined.

In the ratio method, the concentrations of the components in the unknown cannot vary very much from their concentrations in the knowns if Beer's law is obeyed and used. For wide composition variations, working-curves of absorbance ratios "R" vs concentration ratios must be plotted from scans on knowns and then the concentration ratios can be easily read from the curve for the unknowns, once their R values have been measured. Such working curve preparation is necessary, since the absorptivities of the absorption bands of the components of mixtures normally met with, where the ratio method is necessary, are usually not constant over wide composition variation. And they are not constant normally because of "chemical deviations" from the Beer-Lambert law. These "chemical deviations" arise because of the small but significant effect of intermolecular and sometimes even intramolecular "reactions," which affect the ability of a specific vibration to absorb infrared radiation as the immediate surroundings of the chemical grouping giving rise to that vibration change significantly in character.

Component ratio methods find application to co- and terpolymer analysis, materials such as polymeric compositions which can be hydraulically or otherwise pressed into films of useful but indeterminate thickness, melts, and the like.

The accuracy of quantitative ratio methods depends principally on the accuracy to which the composition of the standard mixture can be prepared with uniformity, assuming that the B-L law is obeyed or that a working-curve has been prepared covering the compositional range to be encountered in unknowns.

Pressed Disk Technique. The pressed disk technique can also be used for quantitative infrared analysis of insoluble materials which can be reduced to a finely divided state. Introduced by Schiedt⁸¹ and Stimson⁸⁶ the procedure is often referred to as the halide disk or KBr pellet technique, since KBr is most commonly used. Some other halides, such as KI are also in

use. Investigators are currently seeking other materials as substrates in this method.

While insoluble materials, whenever such is possible, can be reduced to a finely divided state, normally they are more or less opaque to radiations having wavelengths smaller than their diameters, as clearly pointed out by Pfund.⁷² This fact derives from reflection and refraction losses when an assemblage of irregularly shaped and sized particles is irradiated by an infrared beam of wavelengths shorter than the particle diameters. Such losses reduce greatly any rays of infrared which get into the entrance slit of the spectrometer. Moreover, Rayleigh scattering, a phenomenon which occurs when wavelengths larger than particle diameters impinge upon an assemblage of finely divided material, depends among other factors on the difference in refractive index at the phase boundary between particles and air. Since the refractive index of air and practically all solids is quite different in magnitude, Rayleigh scattering further reduces the quantity of radiation that gets into the spectrometer entrance slit when an infrared beam irradiates an assemblage of particles. Since most quantitative infrared work is carried out in the 2 to 16 μ region, there will be rays larger than the particle diameters of finely divided solids.

For these reasons it is desirable to disperse the finely divided solid for quantitative infrared work into a material which is infrared transparent, easily ground, shows good plastic deformation of flow, will form a visually transparent, smooth surfaced, self-supporting whole, and have a refractive index as similar to that of the solids under examination as possible. KBr meets these requirements best of those materials thoroughly studied to date, but KCl and KI are preferred for certain samples.

Since the thickness (path length) of the disk prepared can be measured quite accurately with a micrometer, quantitative work can be carried out directly using the Beer-Lambert law or working-curves when necessary. When both unknowns and the known mixtures are prepared in the same die under the same conditions, the product of concentration and thickness is constant and independent of pressing time for disks prepared from the same weight of sample, if no material is lost in the operations following the weigh-outs.

Quantitative analysis employing the pressed disk technique should be used normally only for those mixtures for which a suitable solvent cannot be found. The solution technique is the preferred one whenever possible, since it is free of most of the difficulties encountered in any solid state technique. These latter include scattering, Christiansen effect, polymorphic form, and uniformity of sample.

The pressed disk technique has certain other annoyances which place limitations on its usefulness. The great hygroscopicity of KBr and other

materials currently in use as substrates makes it very difficult to keep the halide dry and free of absorptions near 3 and 6.1μ arising from OH str and OH bending vibrations of the moisture picked up. Moreover, the sample needs to be very dry or its adsorbed moisture may fog the disk and contribute the annoying water bands mentioned. Another difficulty is a change of polymorphic form of a substance under the influence of the heat developed during grinding and the application of considerable pressure in the pressing operation. This polymorphic form change may occur unbeknown to the investigator and may be only partial and non-reproducible. A third difficulty is that chemical reaction may take place between the sample and the KBr. Thus halide exchange, e.g., can occur in certain cases involving a halogenated sample.

Internal Standards. A few quantitative infrared analytical methods have been developed using internal standards. For example, a weighed amount of an internal standard can be incorporated into a mull preparation and ratio methods used. In general, the use of internal standards leaves much to be desired in the matter of quantitative accuracy and is only to be recommended when no better procedure is applicable. The internal standard needs to possess one or more strong absorptions at wavelengths not interfered with by the components of the mixture under analysis. Spectra of each component to be determined are obtained, incorporating a known quantity of the internal standard, and similarly for the unknown mixture. The choice of internal standard must be made separately for each analysis under consideration. Such materials as lead thiocyanate and hexabromobenzene have been used as internal standards.

Melts. For certain quantitative analyses, melts can be used when solution techniques are impossible and when the unknown mixture can be made molten without any chemical reaction, degradation, or decomposition occurring. Since it is difficult to measure sample thickness accurately on films solidified from the molten state directly between salt plates, ratio methods are usually used with melts. A wedge-shaped cell has also been successfully employed for quantitative work on mixtures by the melt technique. The idea behind the wedge-shaped cell is that the cell can be moved in the infrared beam area so as to adjust the sample thickness to be the same for standards and unknowns. The same thickness is secured each time by adjusting the wedge-shaped sample in the beam until the A 's are equal at some wavelength where there is only generalized absorption and no specific absorption of any of the components. Normally a λ in the 2 to 4μ region is chosen for this purpose. In a typical wedge-shaped cell the path length may be 0.00 at one end of the wedge and 0.127 mm (0.005 in.) at the other. It should be emphasized that melt methods and wedge-shaped cells are limited to a few specialized analyses where other procedures of higher

quantitative accuracy are not possible. Or the accuracy required of the quantitative analysis may not be high. For example, a component may be required in a formulation anywhere in the range from 8 to 12% by weight. In such case, the accuracy obtainable by a wedge method could suffice.

Films. For certain polymeric mixtures it is possible to prepare thin films suitable for quantitative infrared analysis through use of pressure alone or heat plus pressure. Provided such is also possible for the individual components of the mixture, quantitative analysis using Beer's law is possible, since the film thicknesses can be measured quite accurately by taking an average of micrometer readings over the area which will be seen by the infrared beam. For some insoluble polymers, this film approach is the only way in which quantitative infrared analysis can be done.

Aqueous Solutions. Quantitative analysis limited to a relatively few materials can be done in water solution.^{33,75,84,85,92} Such procedures are used when water is the only possible solvent. Quite concentrated solutions are required, so the individual components and the mixture of unknown quantitative composition must have appropriate solubility in water. The region from about 6.5 to 9 μ is normally the only range in which quantitative work can be done because of the strong 3 and 6.1 μ bands of water at the path lengths required.

A BaF₂ cell of about 0.025 mm thickness can be used. Wide slits are employed and the absorption of water in the 6.5 to 9 μ region compensated for by a transmission screen in the reference beam. Concentrations in the 10% range are needed for aqueous infrared spectra.

Biological systems are aqueous ones. The greatest advantage of water solution studies by infrared is the possibility of examining biological fluids in their natural surroundings. Studies of blood,⁸⁵ urine,⁸⁰ albumin, etc. have been initiated. They are likely to become an important research and clinical control tool in the future.

Other typical applications involving aqueous systems include the analysis of metal salts of organic acids, and direct analysis of the water phase of an organic-water two-layer system.⁷⁷

Because inorganic ions yield broad bands in the solid state and even broader ones in water solution, study of aqueous systems of inorganics may not be very rewarding.

Differential Analysis. Whenever feasible or necessary, the accuracy of a quantitative method can be improved by means of differential infrared spectroscopy. A solution of the material under analysis, the concentration of which is known exactly, is placed in the reference beam of the spectrophotometer. The reference beam solution concentration is selected to be somewhat less than that expected in the sample under analysis in the sample beam. This technique, therefore, increases the absorbance ordinate per unit

concentration change, because the absorption band recorded by the spectrophotometer is the result of the difference between the unknown concentration and the known concentration. With ordinate scale expansion available on commercial instruments, this "difference" can be increased up to 20 times for greater accuracy in reading A values. The second factor which increases the accuracy is the increased precision with which the I_0 can be located, made possible because the absorption band to be measured has been enlarged while the background has not. For best precision in quantitative differential spectroscopy, the transmission of the reference beam sample should be in the range of 25 to 50%, with the ideal about 37% as previously indicated. In quantitative differential spectroscopy, careful attention should be given to heating effects which are more pronounced than when air is the reference beam. Both sample and reference cells should be given the same cleaning, filling, and spectrophotometer retention time in order to cancel out any heating effects. Thermostated equipment is best.

Quantitative Infrared Analysis — General Remarks

Quantitative infrared spectroscopy is the procedure of choice only when it is the most accurate and most desirable from a time standpoint or when it is the only possible procedure. There is no justification for using a quantitative infrared method when another, more accurate, less time-consuming method involving classical analytical methods or other instrumental techniques is available. The investigator should not overlook the possibility that some preliminary physical or chemical separation of the components of a complex mixture may result in making the development of a simpler and more accurate quantitative infrared method feasible. And it is not necessary that every component of a multicomponent mixture be analyzed by one method. Certain components may best be determined by titration, thermochemical analysis, potentiometry, polarography, ultraviolet, or mass spectroscopy. One can resort to gas chromatography for reducing the number of components which must be quantitatively analyzed by infrared. The investigator, then, should carefully explore a quantitative situation with which he is faced and select that method or combination of methods which will give him results of the accuracy and precision required with the least expenditure of time. Quantitative infrared spectroscopy is just one of the valuable tools in the arsenal of the analyst.

SHIFTS IN GROUP FREQUENCIES

The successful solution of structural problems involving molecules of industrial interest by means of empirical infrared spectroscopy depends very largely on the validity of the concept of group frequencies. In the

various spectra-structure correlation charts referred to earlier in this chapter, the correlations are not of equal value. Judiciousness in their use is a *sine qua non*, as the authors of these charts have carefully made clear. Practically none of the ranges given for characteristic group frequencies cover all known findings reported in the literature. The correlation chart compilers have purposely limited the group frequency ranges, and rightfully so. Otherwise, many of the ranges which would be presented would be meaningless, for they would cover a very extensive range if account were taken of all known instances in which interaction effects or other interferences occur.

The approximate vibrational frequency undergone by a pair or small group of atoms is primarily dependent on the strength of the bonds among them as measured by the force constant, on the masses of the atoms, and by their geometrical arrangement in space. In any but the simplest diatomic molecules, there is more or less modification through the interplay of "other variables." The precise vibrational frequency is the resultant of all the factors mentioned above.

What are these "other variables"? They can be conveniently divided into external and internal ones. The external ones, concerned with the external environment of the vibrating group, include changes of phase, changes in crystalline form (polymorphism), the presence or absence of hydrogen bonding, and the effect of solvents. The internal factors, operating along the bonds between the atoms or occasionally across intramolecular space, include changes in the geometry or masses of substituents, mechanical coupling between one vibration and another, steric strain effects, and electrical effects.

The importance of these "other factors" is immense because they lead, e.g., to the distinctions between the carbonyl frequencies of anhydrides, esters, acids, ketones, aldehydes, etc., enabling the investigator to determine the class or classes of compounds present in an unknown material from interpretation of its infrared spectrum. In fact, practically any use to which infrared spectra can be put derives from these "other factors." Though the differences they make are minor, their importance is almost in inverse ratio.

The vibrations of multiple bonds and of hydrogen atoms give rise to the most characteristic group frequencies because they are least sensitive to either mass or coupling effects. The $\text{C}\equiv\text{C}$ bond, e.g., as pointed out by Lord and Miller⁶³ and the $\text{C}\equiv\text{N}$ bond from the work of Whiffen⁹⁰ are essentially mass insensitive. In general, no matter what chemical groupings are attached to the acetylenic or nitrile bonds, very little change is observed in the absorption frequency of these multiple bonds. This would be predicted on the basis that the very large bond strengths of triple bonds, and hence high force constants, would effectively localize the frequency, making it

relatively immune to the influence of substituents. Then again, only one substituent is possible for a true nitrile and only one for each carbon in the acetylenic case. Hydrogen is unique from a mass standpoint from other atoms normally encountered in infrared work. Accordingly, X—H str and deformation modes consist essentially only of motions of the hydrogen atom. The heavier element X moves very slightly by comparison, so that such hydrogenic frequencies give rise to highly characteristic group frequencies.

Phase Changes, External Factors

While vapor phase molecular association does occur in a few instances, normally, molecules in the gaseous state can be considered to a first approximation to be free from the influence of other molecules.

In the liquid and solution states, a vibrating chemical grouping of concern to the spectroscopist is surrounded by other like molecules or solvent molecules which may affect its frequency either through molecular association or through changes produced in the dielectric constant of the total medium. Thus, while the vapor phase frequency of the carbonyl str in acetone is observed about 1742 cm^{-1} , it falls to about 1718 cm^{-1} in the liquid state.⁸ The largest factor in this frequency decrease is probably the result of the

loose associations formed of the type $\begin{array}{c} + \quad - \\ \diagup \quad \diagdown \\ \text{C} - \text{O} \end{array} \dots \begin{array}{c} + \quad - \\ \diagup \quad \diagdown \\ \text{C} = \text{O} \end{array}$ in which the separate molecules are linked in chains by electrostatic forces. The loose association is formed from the attractive forces set up between the individual $\begin{array}{c} + \quad - \\ \diagup \quad \diagdown \\ \text{C} - \text{O} \end{array}$ dipoles. Each positive charge induces a small additional negative charge in the oxygen atom of the neighboring molecule, increasing the polarity of the negative link. An increased contribution of the $\begin{array}{c} + \quad - \\ \diagup \quad \diagdown \\ \text{C} \cdots \text{O} \end{array}$ resonance form results, so that the bond lengthens and the carbonyl frequency decreases.

Upon changing from the liquid state to the solid state, owing to the further increase of intermolecular forces, relatively small frequency shifts occur, except where hydrogen bonding is involved. Owing to the increased order of the system, however, some bands, and therefore absorptions, will have disappeared, but in some cases new bands will be observed. The disappearance of rotational isomerism, which is possible in liquids and vapors, in the crystalline state accounts for the disappearance of absorptions arising from less stable isomers. The useful group of bands observed in the spectra of crystalline fatty acids, however, are absent in the liquid

state, since the all-trans arrangement of the methylene groups occurs only when the acids are in the crystalline state. These bands occurring in the region from about 1350 to 1150 cm^{-1} are useful for distinguishing between saturated fatty acids of different chain lengths, as well as fatty acid salts.

Additional bands appearing in the spectra of solids can arise from the increased molecular rigidity resulting from the strong intermolecular forces existing in the crystalline state. For example, in-phase and out-of-phase vibrations of the same chemical grouping in two "identical" molecules of the unit cell can lead to the splitting of a single band in the liquid state into two in the solid state. The well known doublet of crystalline polyethylene at about 725 cm^{-1} , arising from the $(\text{CH}_2)_n$ rocking vibration, is an example. The seemingly "identical" molecules are different because of their different geometrical orientation within the unit cell of the crystal. An estimation of crystallinity can be made reasonably accurately in polyethylene and polypropylene (see Chapter 8) and other polymers, e.g., by making use of bands which are crystallinity sensitive.

A change in crystalline form (polymorphism) leads to observed spectral differences. The red shade and green shade of copper phthalocyanine blue yield different infrared spectra,⁵⁵ as do the blue and yellow shades of Para Red. The reason for the spectral differences is the altered environment of the vibrating groups in the different crystalline forms. These spectral differences are observed, of course, for both organic and inorganic polymorphs. To determine whether one is confronted with polymorphism is simple. If identical infrared spectra are obtained on two materials in the solution state, but different spectra obtained when each is scanned in the solid state, then one has two polymorphic forms of a substance. Quantitative methods can be set up for determining the percentages of the different polymorphic forms present in a mixture of such.

The pressed disk alkali halide technique can give rise to spectral differences as compared to, e.g., mulls, owing to interactions between sample vibrations and those of the alkali halide lattice.

While some of the factors involved which produce spectral changes upon phase changes are known, as suggested above, much further work remains to be done to explain all the numerous small and large spectral changes observed on proceeding from one phase to another.

Hydrogen Bonding. While hydrogen bonding is only one specific type of molecular association, the frequency of occurrence of the hydrogen atom in molecules and its importance to molecular structure set it apart for special consideration. Moreover, it has been studied in greater depth and detail than other molecular association phenomena.

The presence of hydrogen bonding in a molecule produces a shift in the hydrogenic stretching vibration and its overtones to lower frequencies. This

$\Delta\nu$ (shift) is a good measure of the force constant of the hydrogen bonds formed as quantitated first by Badger.² He derived an expression allowing the calculation of such bond energies from the frequency shifts observed.

Later investigations by Lord and Merrifield,⁶² Nakamoto *et al.*⁷⁰ and Pimentel and Sederholm⁷³ showed an inverse relationship between OH frequency shifts and O...O distances valid, provided the bonds are co-linear and not bent. The equation derived is

$$\Delta\nu = 4.43 \times 10^3(2.84 - R) \quad (2-13)$$

where R = the O...O distance. The above equation does not, of course, apply when the O atoms are widely separated, as in the case of very weak hydrogen bonds.

The $\Delta\nu$ resulting from hydrogen bonding can be readily observed. The absorption spectrum of a simple alkanol, say ethanol, in very dilute solution, in a nonpolar solvent like CCl_4 shows a narrow band in the 3600 cm^{-1} region arising from the non-hydrogen bonded (called "free hydroxyl") OH str vibration. Straight ethyl alcohol yields a broad band in the 3300 cm^{-1} region. At intermediate concentrations of ethanol in CCl_4 both absorption bands will be observed in proportion to the concentration of "free" and "bonded" hydroxyls present.

Spectral correlative studies have been made on $\text{OH} \cdots \text{N}$, $\text{OH} \cdots \text{Cl}$ and other types of hydrogen bonds, in addition to the extensive work on $\text{OH} \cdots \text{O}$.

Hydrogen bond frequency shift studies have been used to determine the probable configurations of geometric isomers^{59,45} as an aid in conformation studies on molecules such as DNA,²⁶ the energy of the hydrogen bond in a number of molecules,⁷⁴ and for the determination of the heats of mixing of materials which do hydrogen bond, e.g., the work of Tamres⁸⁹ *et al.* on *d*-methyl alcohol.

Frequency changes resulting from hydrogen bonding can occur in regions of the spectrum other than the X-H str and deformation ranges. Such occur when an X-H frequency is mechanically coupled with another vibration, such as an OH deformation coupled to a C=O str vibration in carboxylic acids. An analogous example applies, e.g., to certain hydroxyl- or amino-anthraquinones.⁵⁶ While AQ itself shows a lone C=O absorption at about 1675 cm^{-1} , 1-OH AQ shows two carbonyl absorptions, one arising from the carbonyl involving carbon 10 at the normal 1675 cm^{-1} frequency, another arising from the carbonyl involving carbon 9 at about 1625 cm^{-1} . Owing to the very strong hydrogen bonding ($\text{O}-\text{H} \cdots \text{O}$) formed between the oxygen of the carbonyl and the hydroxyl in the 1-position, this carbonyl bond is weakened and takes on some single bond character, thus decreasing the carbonyl frequency from 1675 to 1625 cm^{-1} .

Solvent Effects. Ideally, all infrared spectra would be run in the vapor state at low pressure, where molecular interactions would be at a minimum. Obviously, this is impossible for most large molecules of industrial interest. Solution and solid state spectra become a necessity. Insofar as possible, spectra should be run in dilute solution in non-polar solvents. Owing to inherent absorptivity limitations "dilute" solutions are not always feasible, and owing to lack of solubility, polar solvents are sometimes required. As concentration of solute is by necessity increased, and as the polarity of the solvent is increased for the same reason, the effects of solute-solvent interactions are increased.

When possible, dilute solution spectra should be scanned in CCl_4 (5000 to 1600 cm^{-1}), tetrachloroethylene (1600 to 1400 cm^{-1}), and CS_2 (1400 to 650 cm^{-1}) by solvent compensation technique when desirable. This covers the principal spectral region over which the majority of infrared investigations are carried out.

The effects of solute-solvent interaction are usually rather small unless hydrogen bonding is involved. Usually plain str frequencies are lowered, while corresponding bending frequencies are increased, in the solution state as compared to the vapor phase spectrum. There are exceptions. Kirkwood⁵⁸ and Bauer and Magat⁵ developed a theory and equation to explain solvent-induced shifts in frequency. Extensions of the theory and mathematical relationships have been made by Pullin⁷⁸ and by Buckingham.²⁰ Tests of the theory have been carried out in extensive research, particularly by Josien⁵² and her collaborators. The theory has been found to be inadequate in many cases.³⁷ It is evident that all the factors operating in solute-solvent interactions are not known and that too simple a physical model has been used in developing the mathematical relationships. Hallam³⁸ presents a large number of useful literature references to solvent effects on group frequencies broken down by vibration type and vibrating group.

Experimental data on solvent effects are useful despite the inadequacy of theory and quantitative treatment. Questionable frequency assignments can sometimes be tied down by observing whether the band in question shifts in solution as expected. Bellamy and Rogasch¹⁵ pointed this out aptly in distinguishing between 1650 cm^{-1} and 1590 cm^{-1} (the correct assignment) for the carbonyl absorption in 4-pyridones and in reassigning the $\text{C}=\text{S}$ str frequency.

Solvent variation can sometimes provide information on the polarity of bonds, not only for organic molecules but also on ligand bonds in metal complexes.^{1,4,69} Frequency shifts upon change of solvent are sometimes accompanied by relative intensity changes brought about by changes in the ratio of isomers, e.g., when rotational isomers are involved.

Phase Changes, Internal Factors

Mass and Coupling Effects. The substitution of one element for another in a functional chemical grouping always introduces other variables than that of mass. These other variables are usually electrical in character. Therefore, it is difficult to isolate the "mass effect." For example, introduction of a one atom change in a vibrating group may alter not only the mass but also the probability for mechanical coupling to occur. Thus, an observed frequency change will be larger than expected on the basis of a mass change alone.

As mentioned earlier, hydrogenic str and deformation modes and multiple bond vibrations are the most apt to be mass insensitive. Halford³⁶ showed that with molecules of the type X_2CO , the mass of X can be changed from 12 to infinity without changing the carbonyl frequency more than 25 cm^{-1} . When the mass gets below 12, however, strong coupling occurs between the C—X str modes and the carbonyl frequency in the 1700 cm^{-1} region, the symmetric and asymmetric str frequencies are widely separated, hence, no isolation of a purely mass effect is possible.

Herzberg⁴¹ and more recently Lord and Miller⁶³ have aptly explained the conditions under which coupling of two vibrations occurs to yield frequencies which are abnormal. Coupling of two vibrations takes place when two conditions are fulfilled: (1) the vibrations are of reasonably high and nearly equal frequency; (2) they have the same symmetry.

Many vibrations arising from the coupling of two nearby vibrations nonetheless are useful in spectra-structure correlation work. So long as the coupling environment remains constant, then useful group frequencies arise. Frazer and Price³⁰ pointed out that two highly characteristic and useful absorptions of open chain secondary amides, $RCONHR$, arise from coupling NH deformation and C—N str frequencies. Hadzi and Sheppard³⁵ showed that C—O str and OH deformation vibrations of carboxylic acids are coupled, but since the $RCOOH$ environment remains constant, they are useful group frequencies.

Since absorptions arising from coupled vibrations cannot be assigned to one specific vibrating group, factors which change the "constant environment" will affect the frequencies of both vibrations contributing to the coupling.

Uncertainties in vibrations involving hydrogen, where coupling is a possible cause, can often be unravelled using deuteration techniques. The help given by deuteration follows from the great mass difference between H and deuterium. When neither the X—H nor the X—D frequencies are involved in coupling effects, the frequencies should be related by $1 : 1, \sqrt{2}$.

If either the $X-H$ or $X-D$ frequencies are involved in coupling, then such frequencies will be observed not related by $1 : 1/\sqrt{2}$.

Strain Effects. When the normal bond angles of the groups about a carbon atom are changed as enforced by ring or steric strain, changes in the vibrational frequencies result from the alterations in the bond lengths produced. The familiar tetrahedral angle disposition of four groupings attached to a saturated carbon atom arises from the sp^3 hybridization of that carbon. The planar trigonal distribution about an olefinic carbon arises from sp^2 hybridization. The s orbitals are spherical in contrast to the cylindrical p orbitals. Normally s orbitals are shorter than p orbitals. Changes in the proportions in which s and p orbitals are mixed, therefore, result in changes in the bond lengths and hence in the vibrational frequencies.

Alkane $C-H$ str frequencies are observed in the 2965 to 2850 cm^{-1} range. Cyclopropane, however, shows $C-H$ str frequencies near 3030 cm^{-1} . Ring strain has reduced the normal tetrahedral angles about the saturated carbon atoms. The p orbital portion of the $C-C$ bonds has increased and therefore the $C-H$ bonds have more s character, i.e., are shorter. The accompanying frequency increase raises the $C-H$ str to 3030 cm^{-1} .

Vibrations involving double bonds show the largest strain effects. For unstrained six-membered rings, e.g., the >C=C< frequency is normal as shown by the 1646 cm^{-1} value for cyclohexene.⁶⁴ For larger rings, this frequency is also normal, evidently because the greater space occupied by the ring system allows adjustments to be made which relieve strain. Decreasing the ring size below six, however, gives rise to unrelievable strain and the >C=C< frequency decreases: cyclopentene absorbs at 1611 cm^{-1} and cyclobutene at 1566 cm^{-1} .

The attachment of a second ring increases the strain and the >C=C< frequency decreases further. Why this happens is not known.

Strain effects like those mentioned above occur also in the more complicated steroids,⁴⁸ triterpenes,²³ etc.

As expected, the $C-H$ str frequencies increase as the $C=C$ frequencies decrease. The cyclohexene $C-H$ absorbs at 3017 cm^{-1} , while, e.g., that in cyclobutene absorbs at 3060 cm^{-1} . The behavior of the CH out-of-plane deformation frequencies has so far not been clearly explained.

Exocyclic methylene groups show a rise in frequency as the ring size diminishes, since here the C^1-C bonds are distorted, take on additional p -character, and leave the olefinic bond with more s -character. The bond length is reduced and therefore the frequency rises.

Carbonyl absorptions in ring systems behave practically the same as exocyclic methylene groups. Rings having more than six members can make adjustment to reduce strain and show normal frequencies, but in the five-membered rings of, e.g., anhydrides, lactones, and lactams, higher carbonyl frequencies are observed than for the corresponding open-chain compounds. Four-membered rings show a still greater frequency increase. Halford³⁶ has successfully explained the situation on theoretical grounds.

Carbonyl frequencies are also affected by ring fusion. The penicillin studies during the early 1940's revealed that β -lactams fused to a five-membered ring absorbed at higher frequencies than those which were not. Similarly, cyclic ketones having carbonyl bridges in six-, seven-, and eight-membered ring systems reflect the additional strain by yielding higher carbonyl frequencies.

Strain arising from purely steric effects has not been sufficiently studied. Orr⁷¹ and Bellamy⁹ find the principal effects of steric strain to be reflected in band width variations rather than in frequencies. Here may be a fertile field for some investigator to discover a useful relation between steric hindrance and band widths that may solve some puzzling molecular structure problem.

Electrical Effects

The term electrical effect covers the inductive, resonance, and field effects operating in the immediate locale of a vibrating group. All these change the hybridization of the atoms on which they operate, but they are more strictly local than steric effects. Understanding of how these electrical effects operate on vibrational frequencies is fragmentary, primarily because they are usually very difficult to isolate and sometimes work in opposite directions. They can be studied only in groupings which are insensitive to mass or coupling effects and under similar conditions of association, etc.

Electrical effects, however, can play a useful role in the checking of vibrational assignments, as a means of confirming a provisional identification of a band by reference to the precise position of another, and in finding relationships involving many bands within one spectrum. Bellamy and Williams¹⁶ were able to obtain reasonably good agreement over a fairly wide range of differently substituted methyl compounds for the six fundamental methyl group vibrations, using plots of mass-corrected $\text{H}-\text{X}$ str frequencies against CH_3-X frequencies (where $\text{X} = \text{H, halogen}$). Thus, using only the OH str frequency of water, the six fundamental methyl group frequencies can be read from their plot. Similarly for other compounds in the $\text{CH}_3-\text{X(H)}_n$ series.

Jones and Sandorfy⁴⁶ found a linear relationship between the carbonyl and $\text{C}-\text{O}$ str frequencies of steroid acetates, valuable in identification work.

The usual mass sensitivity of the C—O grouping is minimized in such molecules by its constant environment. Its frequency, therefore, as well as that of the carbonyl group, varies systematically with the electrical character of the substituents.

Inductive Effects. A change in frequency of a vibrating atom pair brought about by a change in the electronegativity of a substituent is known as the "inductive effect." The electronegativity change alters the polarity and therefore the frequency. This inductive effect operates only along the bonds, is independent of geometrical arrangement, and is primarily dependent upon the effective electronegativities of the substituent atoms or groups.

All covalent bonds showing absorption in the infrared possess some degree of polarity. While the oxygen molecule, e.g., contains a rather pure covalent link, it is inactive in the infrared. Consider the changes in carbonyl frequency on going from acetone to acetyl chloride. The carbonyl linkage in acetone has some polar character and the oxygen atom possesses some negative charge. The electron cloud forming the bond is displaced towards the oxygen. Replacement of one of the methyl groups by a much more electronegative substituent, say chlorine, will pull the electron cloud back a little nearer to the geometric center, owing to the increased electron attraction. The polar character of the carbonyl link diminishes; the vibrational frequency rises.

Frequency shifts arising from inductive effects will depend essentially on the electronegativities of the substituents. When only induction is involved, then a direct quantitative relationship between frequencies and electronegativities should prevail.

Bellamy¹⁰ has shown for simple molecules XH_n that the $X-H$ str frequencies (corrected as necessary for minor mass effects) plotted against Pauling electronegativities yield a simple linear relationship for monovalent elements and similarly for multivalent elements. For the latter the lines are displaced to one side, depending on the valency state. Thus, factors in addition to electronegativity are involved for multivalent elements. The most important of these may be angle effects, since $X-H$ frequencies in these cases are not single but composed of asymmetric and symmetric modes.

Goulden³⁴ found a linear relation between the OH str frequencies of monomeric alkyl acids and their pK_a values. This result shows the pK_a value of these acids, the measure of the relative ease of ionization of the hydrogen atoms, is a measure of the inductive effect of the group R (in $RCOOH$). While only induction is involved in the case of the alkyl acids, in aromatic acids both inductive and resonance effects are operative. Therefore, a different linear relation is observed between pK_a values and OH frequencies, the difference in slope arising from the additional effect.

Bellamy¹² observed a linear relation between CH_2 deformation frequencies and the sum of the electronegativities of the substituents in vinyl compounds of type $\text{CH}_2=\text{CXY}$ for alkyl or halogen groups. For oxygen or nitrogen substituents, however, the relation failed, owing to the appreciable influence of resonance as an additional variable.

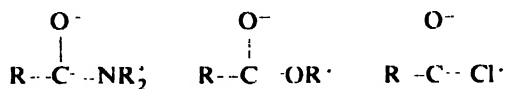
Bell *et al.*⁶ showed that in phosphoryl halides the $\text{P}=\text{O}$ frequency is a linear function of the sum of the halogen electronegativities. Here, non-planar pyramidal structures are involved, the resonance factor is much reduced, and inductive effects are the principal influence.

While the study of the relation between inductive effects and group frequencies can on occasion be very useful, by providing a measure of the strength of induction, results of such studies must be examined critically, for understanding of those situations in which inductive effects only are operative is very incomplete.

Conjugation and Resonance. In a simple conjugated double bond system, a slight lengthening of the double bonds occurs through the influence of the mobility of the electrons leading to a decrease in the $\text{C}=\text{C}$ frequencies. The mobility of the electrons arises because the π clouds of multiple bonds are somewhat polarizable and molecular orbitals are formed which include all the carbon atoms, as in 1:3-butadiene, e.g.

When an element containing easily polarizable electrons in the form of lone pairs is attached to a multiple bond, effects are observed owing to the contributions of canonical forms resulting from resonance. These resonance effects contribute to the final bond state, as do the electronegativities of the substituents. The effect is greatest with nitrogen substituents, somewhat less with oxygen, and least with halogen substituents, as expected on the basis of the decreasing ease of polarizability of these atoms.

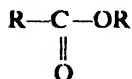
For amides, esters, and acid chlorides, contributions of canonical forms such as



influence the carbonyl frequencies in addition to the electronegativities of the substituents. They tend to lower the frequency because of the increased $\text{C}=\text{O}$ bond length.

The atom with the available polarizable electrons directly attached to a multiple bond must lie in a common plane for resonance effects to occur. For example, in the nonplanar system diallyl sulfoxide, the $\text{S}=\text{O}$ frequency is unchanged.¹¹ Furthermore, resonance effects cannot be isolated from the inductive effects contributed by the same substituents, so that inductive (I) and resonance (R) effects must be considered in combination.

It is a well-known fact that the carbonyl absorptions of vinyl esters are observed at significantly higher frequencies than normal esters. Bellamy suggests this observation may be explained by the cancelling out of the "mesomeric pull" upon the oxygen lone-pair electrons by the competing carbonyl and vinyl groups. Thus there is no resonance. The carbonyl frequency is determined only by the effective electronegativity of the OR group in the molecule,



Since the resultant of I and R effects determines primarily changes in acid and base strengths, dipole moments, bond lengths, and sometimes reaction rates, a number of attempts have been made to evaluate these effects quantitatively, using group frequency shifts. Several attempts have been successful because the group frequencies selected were quantitatively dependent only on I and R effects. Examples are the strengths of acids, the basicity of primary amines related to their NH str frequencies, and the relation of carbonyl frequencies to polarographic half-wave potentials,¹² redox potentials,⁵³ bond lengths,²⁷ and to the stabilities of chelates.¹⁴

In the important field of reactivity studies, some success has ensued in relating group frequencies to reactivities. Both dynamic factors and static factors control reactivities. The dynamic factors, termed electromeric effects by Ingold, involve such factors as the change in electron distribution within a molecule by the approach of an attacking reagent. No spectroscopic measurement made on the undisturbed molecule in the ground state can reflect this dynamic influence. The static factors involved in reactivities are induction and resonance, and in certain situations they alone control reaction rates. Such reactions are usually found in aromatic chemistry, and most particularly in reactions involving attack on ring substituents. Hammett's³⁹ original and extensive work on reactions of this type has been extended by Jaffe,⁴⁴ Taft,^{87,88} and others.

Hammett developed the σ value, a constant which measures the electron-donating or electron-withdrawing powers of a substituent. He showed that a specific group in a given position in an aromatic ring will exert a constant effect upon the reactivity of the compound, dependent upon its inductive and mesomeric properties. These Hammett σ constants apply to a wide range of different types of reaction and are additive. The reactivity of a doubly substituted aromatic can be predicted from the arithmetic sum of the group σ values.

Many studies have been carried out relating group frequency shifts to Hammett σ values, since the latter provide a convenient measure of the I

and R effects of individual groups in aromatic systems. Bellamy,¹³ e.g., found a linear relation between σ value and the out-of-plane CH deformation modes of aromatic rings. He has also been able to derive σ values directly from observed frequencies. For example, using a plot of H-X str frequencies vs Pauling electronegativities, the σ value of the *t*-butyl group was obtained from the appropriate absorption in the spectrum of 1, 3, 5-tri-*t*-butyl benzene.

Linear relations between σ values and group frequency shifts have been established for the NH₂ str frequencies of aniline,^{21,28} the OH str frequencies of phenols,⁴² and the carbonyl frequencies of aromatic ketones.³²

The relation between intensities of absorptions and I and R effects and of the physical properties also dependent on these factors is not yet clear. Sometimes intensity changes parallel group frequency changes and sometimes not. Much further work remains to be done in combining the results of intensity and frequency studies with I and R effects.

Dipolar Field Effects. Field effects are the electrical influence operating on group frequencies in unstrained systems *across* intermolecular space, rather than along the bonds. The frequencies are influenced by dipolar electrical forces in any molecules in which two charged atoms with polarizable electrons occur near to each other in space.

The principal value of the hypothesis of field effects is that it enables a number of otherwise anomalous frequencies to be explained. Jones *et al.*⁴⁹⁻⁵⁰ observed in α -halogenated keto steroids that equatorial substitution raised the carbonyl frequency about 25 cm⁻¹ but axial substitution did not. Since resonance effects should be small in such compounds and induction is independent of molecular geometry, some other effect must be responsible. Jones *et al.*^{47,51} suggested dipolar field effects may be responsible.

This suggestion has been elaborated by Bellamy and Williams¹⁷ in simple electrostatic terms. The near approach of a negatively charged halogen to the readily polarizable negatively charged oxygen of the carbonyl group results in a mutual induction of opposite charges. The negative character of both the chlorine and oxygen atoms decreases, the C-Cl and C=O bonds become less polar, and their vibration frequencies rise, as observed experimentally.

Qualitative and quantitative field effects studies have helped explain unusual frequencies observed in a number of α -halogenated carbonyl compounds, assign the multiple carbonyl absorptions observed in the spectra of open-chain ketones in the liquid state arising from the various rotational isomers present, and quantify the alteration of the C=O bond dipole under the influence of the field effect of the CF₃ group in trifluoromethyl carbonyl compounds. Josien and Calas⁵⁴ in studies on methyl acetate and its chlorinated derivatives in carbon tetrachloride solution used a field effect

explanation to account for a 1775 cm^{-1} ester carbonyl absorption appearing in the spectra of both the mono- and dichloroderivatives. While each of the latter showed a carbonyl absorption at 1750 cm^{-1} , where methyl acetate absorbs under these conditions, they also each gave an additional band at 1775 cm^{-1} , arising from isomers. In the isomers, where the chlorine atoms are turned away from the carbonyl oxygen atom, the 1750 cm^{-1} band arises. When dipolar field effects obtain, the 1775 cm^{-1} band arises.

While field effects are the principal cause of frequency shifts in α -halogenated carbonyl compounds, they are also observed intramolecularly in cyclic ring systems, which enforce close approximation, e.g., of a nitrogen atom to the carbon of the carbonyl group. Here abnormally low carbonyl frequencies are observed. The cyclic aminoacyloins are an example.¹⁸

The further study of the origins of group frequency shifts offers a fertile field for unravelling explanations of the effect of nearest and nearby neighbors of functional chemical groupings on the characteristic group frequencies of those functional groupings. Such new knowledge could greatly increase the ability of spectroscopists to interpret the infrared absorption spectra of unknown substances in terms of molecular structure.

THE LIMITATIONS OF INFRARED SPECTROSCOPY

While infrared spectroscopy is the most powerful all-around technique available for the solution of molecular structure problems and for identifying and quantitatively determining substances, it does have limitations.

Infrared spectroscopy is applicable to all organic materials and to those inorganics possessing polyatomic cations and, or anions or to inorganics having significant covalent character in their chemical bonds. Atoms and monatomic ions in general, however, do not absorb infrared. Thus infrared is eliminated as an analytical method for a number of inorganic problems and for the "inert" gases per se.

For a molecular vibration to be infrared active, i.e., absorb infrared radiation, a change in dipole moment must occur during that vibration. Molecules such as H_2 , O_2 , N_2 , Cl_2 , etc. will therefore not yield any useful infrared absorption spectra because no change in dipole moment occurs during their lone str vibrations, which are electrically symmetrical. Obviously, then, one cannot hope to identify or determine such diatomic molecules by infrared.

It is fortunate that materials such as NaCl , KBr , AgCl , LiF , CaF_2 , CsBr , and the like do not yield characteristic infrared absorption spectra, for because of this they are useful as prisms, window materials, and other optical components.

Since the atoms in a large number of inorganic molecules are relatively heavy as compared to C, H, N, and O, their vibrations have low frequencies. This often puts vibrations beyond the range of the most-used infrared instruments. Since 1960, however, the far infrared region has been opened up for industrial use by the advent of commercially produced spectrometers. In 1965 three different instrument manufacturers offered far infrared spectrophotometers capable of yielding useful spectra out to 35 cm^{-1} (about 285μ).

Another limitation of infrared is the inability to do very much with aqueous solutions because of the extremely strong absorption of water. Capillary thickness (no spacer) spectra of water solutions or aqueous emulsions scanned between AgCl, BaF₂, or "Irtran" plates can yield much valuable information about the nature of solute or emulsion components present. Even at this minimum path thickness, the 3 and 6.1μ water absorptions will obscure OH, NH, and certain carbonyl absorptions one may be seeking. And if the concentrations of components to be identified is very low, their absorptions may not appear at all or be very weak at capillary thickness. While a small number of applications of infrared can be made to concentrated (2 to 10% by weight) aqueous solutions in the 6.5 to 10μ region by appropriate differential procedures, in general, infrared has only limited applicability to water solutions. These few applications can be very important ones, particularly where the concern is pharmaceutical and biological problems.

Except for analytical methods relying on absorptions arising from vibrations involving very highly polar bonds between atoms, the detectability limits of the usual infrared quantitative procedure are not very great. If, e.g., both an ultraviolet and an infrared quantitative procedure could equally well be used, the ultraviolet method should be the choice at low concentration levels, because it would be more sensitive. The much greater range of applicability, however, of infrared methods over UV procedures, and the much greater specificity of infrared makes it often the only possible choice for an adequate quantitative analysis.

Infrared techniques can distinguish between all types of isomers with the exception of optical enantiomorphs. Optical isomers yield identical absorption spectra and therefore infrared studies cannot distinguish between them.

The inability to transfer quantitative analytical methods from one instrument to another, even of the same make and model, as explained earlier, is another limitation of infrared. A spectroscopist setting up an already developed quantitative method on a different instrument needs only to prepare and scan the standards at the given known concentrations, in given solvents, in specified cells of given path length, draw the base

lines, measure absorbances, and set up his own Beer's Law plots or working-curves. This is a time-consuming and therefore expensive proposition. In a multi-plant organization, to transfer a method developed in one location to five scattered plant locations, means essentially the total procedure has to be repeated six times. Fortunately, analyses where accuracy requirements are not high do not fall into this category.

While the statement that no two chemically different substances which absorb infrared radiation will yield identical spectra is normally true, there are a few exceptions. For example, no infrared spectral differences would be expected between the molecules $\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_{21}\text{CH}_3$ over the 2 to 25μ range. In these two molecules, all the functional groupings are the same and the nearest neighbors of any given methylene or methyl group are essentially the same. Therefore, their fundamental region infrared spectra are the same. Possibly, however, conformational differences could be observed in the far infrared.

The spectra of monomers, dimers, trimers, etc. are readily differentiated one from the other, but infrared cannot usually distinguish between two high polymers comprised of the same monomeric units but which differ widely in molecular weight. A polystyrene of 100,000 number average molecular weight, e.g., usually does not differ spectrally from one of 150,000.

While correct interpretation of appropriate infrared spectra can always help, and sometimes yield unique molecular structure determinations of unknown substances, it is vital that the investigator have independent evidence from other physical measurements that he is concerned with a single pure chemical species. Otherwise, when he assesses the significance and meaning of moderate and weak intensity absorptions, he will not know whether an observed absorption arises from the unknown, another component, or an impurity.

Despite the limitations of infrared spectroscopy discussed above, it is, and will continue to be, the most powerful single technique to bring to bear on the solution of molecular structure and chemical identification problems with which the natural scientist may be confronted.

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CHAPTER

3

Instrumentation

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HISTORICAL

Infrared instrumentation has made substantial progress in the 165 years since the discovery of infrared radiation by Sir William Herschel in 1800. The modern infrared spectrophotometer is a marvel of convenience and utility compared to the crude equipment with which the early spectroscopists worked. Considering the obstacles encountered along the path, progress has been remarkably good. One senses a feeling of respect and admiration for those early workers who had to construct for themselves or have especially made, such components as detectors, prisms and gratings, which we now take for granted. Admiration also is due for their patience and diligence in plotting the spectra incrementally, usually in the still hours of the night when building vibrations and other disturbances were at a minimum.

In some cases, progress was contingent on concurrent developments in other fields, such as electronics and optical components and materials. For example, the electronic servo system and an infrared detector fast enough to respond to chopped radiation were prerequisite to a completely practical automatic double-beam ratioing system.

In the course of these developments the returning interest in certain systems is noteworthy. For example, some of the earliest spectrometers used grating dispersing elements. With the availability of large prisms in a range of materials which permitted selection to provide moderately high dispersion throughout the infrared region of interest, gratings were almost

**The Dow Chemical Company, Midland, Michigan.*

completely neglected for about 30 years. During this time multiple prism spectrometers appeared^{4,19,47} as well as multiple spectrometers, each using a different prism material to give wide range coverage with relatively good dispersion. The lag in interest in gratings was largely the result of the inconvenience in their use. The spectroscopist prefers a wide range continuous spectrum free from breaks and overlaps. With the appearance of automatic grating and order changing spectrometers^{3,32,43} and filter grating spectrometers^{1,17} which produce this kind of spectra, preference for the grating instrument is now predominant.

Table 3-1 is a list in chronological order of some of the more significant steps in the development of the modern infrared spectrometer.

TABLE 3-1. CHRONOLOGY OF INFRARED SPECTROMETER DEVELOPMENT

1800	Herschel discovered infrared radiation in the sun's spectrum by observing temperature rise in thermometers with a heat maximum beyond the visible. ³¹
1880	Langley introduced a superior detector using the bolometer principle which facilitated spectroscopic measurements with gratings and prisms.
1897	Restrahien were discovered to provide a means of long wavelength separation which enabled Rubens to extend his investigations to 300 μ . ⁵⁹
1905	Coblentz used a prism spectrometer to demonstrate experimental evidence of the correlation between molecular structure and characteristic absorption and emission frequencies. ¹³
1910	Wood introduced the echelette grating which became an important factor in the design of high performance spectrometers from the far through the near infrared. ⁶⁷
1910	1939 Research carried on principally at universities. Improvements in optical systems, detectors and measuring systems. ^{10 15 16 29 53}
1941	N. Wright pointed out application and techniques for infrared quantitative and qualitative analysis in the chemical industry at The Dow Chemical Co. Spectroscopy Laboratory. ⁷⁰
1945	Introduction of electronic A.C. amplification with short time constant thermocouples and interrupted radiation. ^{9 30 35 57 58}
1947	Development of double-beam ratioing systems carried on for several years by several workers. ^{5 28 41} First widely accepted system appeared at The Dow Chemical Company in 1947. ⁶⁹
1949	1961 Rebirth of grating spectrometers. Many workers recognized advantages of gratings and several instruments were described. They were hindered by operating inconveniences and interrupted spectra presentation ^{17 24 26 44 62 65 69} until the completely automatic prism grating spectrometers with unbroken scans ^{3 32} and the filter grating instruments also giving unbroken spectrograms. ^{1 17}
1964	Extension of filter grating spectrometer principle to 300 μ . ¹⁹

INFRARED SPECTROMETER COMPONENTS

Since an infrared spectrometer is an assembly of a number of individual components such as source, slits, collimator, dispersing elements, detector and various other mirrors, these components and some of their special characteristics will first be considered and then the manner and reason for use in the completed spectrometer should become more apparent.

Infrared Sources and Source Optics

At present the only sources available for continuous coverage of the infrared region of chemical interest are those of the thermal radiation type in which the power radiated is a function of temperature and emissivity. This relation is expressed by the Planck Radiation Law

$$J_{\lambda} \propto C \lambda^{-5} \frac{1}{e^{\frac{C_2}{\lambda T}} - 1} \quad (3-1)$$

A set of curves is shown in Figure 3-1 for the relative intensity vs wavelength for a blackbody at several temperatures. These curves also illustrate the shift of the radiation peak toward shorter wavelengths as the temperature is increased according to the Wien displacement law: $\lambda_m = 2897.2/T \mu$. The curves further show the much more rapid increase in intensity at short,

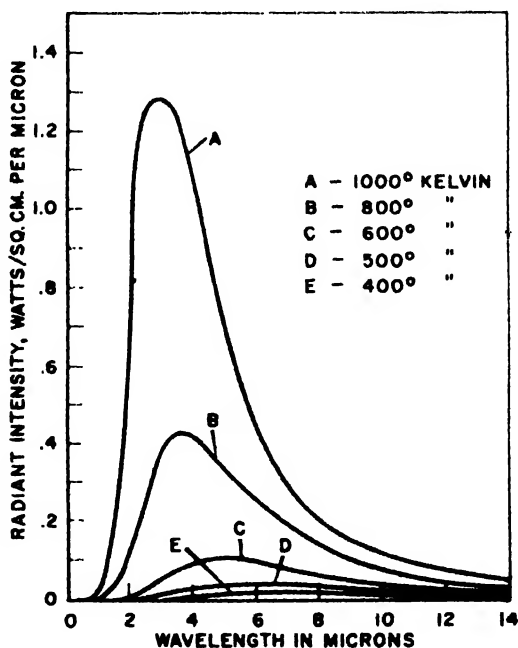


FIGURE 3-1. Spectral radiant emittance of a black body vs wavelength at various temperatures.

as compared to long, wavelengths as the temperature is increased. These considerations quickly lead to the conclusion that a good source should be as hot as possible. However, the temperature at which available source

materials will operate for a reasonable period of time is limited. Furthermore, after attaining the 1500 to 1800 K. operating temperature there is little performance advantage to be gained in the 2.5μ (4000 cm^{-1}) to 25μ (400 cm^{-1}) region by a few hundred degrees increase that might be obtained by a search for other materials or by sacrificing the life expectancy of presently available materials.

Globar. Although earlier infrared spectrometers used the globar (silicon carbide) source almost exclusively, it has some inherent disadvantages which make it probably the least desirable of any of the commonly used sources. It is necessary to keep the contact electrodes relatively cool, and with the globar's negative temperature coefficient, a relatively large proportion of the input power is dissipated in the electrodes. For this reason the globar is usually used with water-cooled electrodes and requires considerable maintenance to retard the formation of high resistance contacts as a result of oxidation.

Heated Ceramic. Another type of source is described in Ref. 33. A ceramic rod is wound with a platinum filament and then coated with a refractory cement. Subsequent experience with the life of these elements has been unsatisfactory and the author herewith wishes to withdraw his recommendation of this type.

A more satisfactory replacement for both the globar and ceramic rod is a close-wound nichrome helix. Operating temperatures and emissivities are nearly equivalent for all three types. The nichrome source does not require water-cooling, requires little or no maintenance and gives long service. The long-wave emissivity does not reach maximum until after aging at the operating temperature for several hours, after which the oxide coating will be formed to its maximum thickness. This source is especially recommended where reliability is essential, such as for a continuous plant stream analyzer. When operated at a somewhat reduced temperature, a life of several years can be expected.

Nernst. One of the most popular sources in use at present is the Nernst filament. It is made of a mixture of rare earth oxides extruded into thin hollow rods with platinum leads fused to the ends.

This is another example of a device which was quite widely used in the earlier stages of infrared developments, then, for a time, interest lagged, but it is now returning to favor. Some of the reasons for renewed interest are that manufacturing techniques have been improved so that the elements are inexpensive and reliable with an average life of six months to a year. They do not require water cooling and the operating temperature (about 1800°C) is the highest of any commonly used infrared sources. The radiation intensity is approximately twice that of the nichrome and globar sources except in the 2μ (5000 cm^{-1}) to 5μ (2000 cm^{-1}) region where the Nernst

has lower emissivity and the radiation intensity here is approximately equal to the lower temperature sources. Because of the high temperature coefficient of resistivity, the Nernst is not self starting and requires a current limiting resistor. This is not a serious disadvantage, since commercial spectrometers using this source have a built-in electrical heater for starting. A very successful method uses the Nernst in series with two parallel tungsten lamps for normal operation. For standby, a relay is used which is controlled by the chopper switch to disconnect one of the lamps but still maintain the source in a conducting state at about half current. With this arrangement the source is first started with a torch and thereafter not permitted to cool below its conducting state. It appears that by avoiding the extreme temperature changes, the service life of the Nernst is actually improved over that where it is allowed to cool completely during the periods when the spectrometer is idle. Some complications have been experienced in adapting the Nernst source for use with the larger spectrometers. The standard Nernst filament can be made in any required length but to avoid current channeling, its diameter is limited to about one millimeter. This requires a magnification of five or more to fill out the entrance slit of the larger spectrometers and introduces some inconveniences in the design of the source optics. There has appeared recently a larger Nernst source element manufactured by a somewhat different technique for the Unicam SP 200 spectrometer. Its size is 20 mm by 2 mm, permitting the use of standard source optics even in the larger spectrometers.

Source Optics. The source optics are the least critical of any in the spectrometer because it is usually possible to work with a source with some excess of area. The requirements are that a source image be located at the entrance slit with adequate size to fill the widest slit to be used. The beam angle of divergence should be of a size which will illuminate an area of the collimator adequate to completely cover the dispersing element. This can usually be accomplished with a spherical concave mirror used somewhat off-axis. Some examples are shown in the optical schematic diagrams of Figures 3-11 and 3-14.

Slits

The slits perform a very important function in determining the resolution of a spectrometer and therefore warrant considerable attention in design and adjustment. Basically the purpose of the entrance slit is to provide a narrow source of light so that after dispersion and refocussing in the plane of the exit slit, the amount of overlapping of the monochromatic images is limited. The exit slit then selects a narrow band of the dispersed spectrum for observation by the detector. In practice it is desirable to have the entrance and exit slits of equal width because it can be shown that for the

conditions of a given resolving power, maximum radiant power is passed by the spectrometer when this is true. Under these conditions the width of a monochromatic image of the entrance slit is such that it will just be passed by the exit slit.

Slit Curvature. Either a prism or grating monochromator with a straight entrance slit, form curved monochromatic images in the exit image plane. This is true in the case of the prism because rays passing through a prism obliquely, suffer greater deviation than the corresponding rays in a principal plane. To a first approximation the spectral lines are parabolic in shape. An approximate formula for determining the radius of curvature of the image at the vertex of the parabola is:

$$\rho = nf \frac{(1 - n^2 \sin^2 \beta)^{1/2}}{2(n^2 - 1) \sin \beta} \quad (3-2)$$

Where n is the prism refractive index, f is the collimator focal length and β is the refracting angle of the prism used at minimum deviation. For a Littrow arrangement where the beam traverses the prism twice, the required radius is half that given by the above formula. Since n is a function of wavelength it is obvious that the required curvature will vary with wavelength, so it is advantageous to calculate the curvature for a region of minimum slit width because the relative error from curvature is inversely proportional to slit width.

Similarly with a grating monochromator, the grating space seems smaller for the rays from the ends of the slit because of their angle of dip or elevation. The lateral displacement of that part of the spectral image which is distant x above or below the center line is given by the relation:

$$y = x^2 / \tan i \quad (3-3)$$

where i is the angle of incidence on the grating (assuming angle of diffracted beam equals i) and f is the focal length. Again the curvature required is a function of wavelength (grating angle) requiring some compromise because in most cases slits with variable curvature would probably be considered an unwarranted elaboration.

In general, it is desirable to have a straight exit slit image in order to accommodate a straight-sided detector receiver. So a straight exit slit is usually used and the curved slit is used at the entrance, curved in the direction in which it counteracts the curving effect of the dispersing element on the exit image. The source image can be made large enough to cover the curved entrance slit so that there is no loss of light at this point. An approximation of the effectiveness of correction for image curvature in the monochromator can be determined by observation of a visible spectral line from a mercury arc source.

Slit Height. Slit height is an additional factor entering into the design of a spectrometer. The absolute power transmitted by a spectrometer is inversely proportional to the ratio of the collimator focal length to the slit height. A compromise must be reached, however, because there are several factors which limit the minimum ratio to about 20 in a practical spectrometer. These limiting factors are:

(1) Loss of light intensity at the ends of the slit image because of masking by other apertures (usually the collimator and dispersing element).

(2) Loss of resolution as a result of imperfect curvature at some wavelengths.

(3) Loss of light at the detector through inability to obtain sufficient demagnification to accommodate a limited area detector.

For best performance it is essential that the slit jaws have sharp, clean edges which are aligned to meet in a plane perpendicular to the direction of the light beam.

Collimators

Next to the dispersing element, the collimator (or plural if two are used) is the most critical element in determining the resolving capabilities of a monochromator. Especially in low dispersion instruments such as those using prisms, a high degree of accuracy is required of the surface figure so that spectral lines will be in sharp focus.

The size (diameter) of the collimator is chosen as required to illuminate the area of a previously selected dispersing element. After selection of the dispersing element we have yet to select the focal length of the collimator which will determine f /number in the relation: f /number = f/D (where D is the diameter). The focal length is important since it largely determines the overall size of the monochromator, but for a dispersing element of a given size the focal length or f /number of the collimator is not of much significance in determining the power transmitted by a spectrometer. This is true because with present detectors and assuming a practical recording speed, performance will be energy limited. If we now compare two monochromator systems, both having the same size of dispersing element but one having twice the focal length of the other, we find the shorter focal length system has twice the solid angle in the input beam. This should give a factor of four in total light flux, but for a given resolution the longer focal length system will have twice the slit height and width, giving a factor of four in slit area and light input. The two systems, therefore, are equivalent in total light flux.

For the dispersing element to function efficiently it is required that the illumination be collimated in a parallel beam. The collimating mirror in a monochromator is positioned so that the slit is located at the focal length

of the collimator. The beam returning from the dispersing element to the collimator is still parallel and so is refocused as a series of monochromatic images of the entrance slit again at the focal length. Since the slit is an extended source in the vertical direction, light in vertical planes contains divergent rays. Light in the horizontal planes is properly collimated for efficient dispersion in the direction of the narrow dimension of the slits.

The optical figure and arrangement of collimators for various monochromator systems will be discussed in a following section.

Dispersive Elements

Prisms. The principal virtue of prisms as dispersive elements for infrared is the relative simplicity of the instrument using them. The entire infrared region over which the prism material is transparent, can be scanned in one continuous sweep of the scanning arm with no auxiliary spectral separating devices.

Refraction by Prism. A ray of light passing through a prism can be traced by applying the law of refraction according to Snell:

$$\sin i = u \sin r \quad (3-4)$$

where i is the incident angle, r is the refracted angle and u is the index of refraction of the prism material. The index of refraction is a function of wavelength as illustrated by the plot of the curves in Figure 3-2. The regions of greatest dispersion for a material are the regions of maximum slope of the refractive index curve. It will be noted that unfortunately

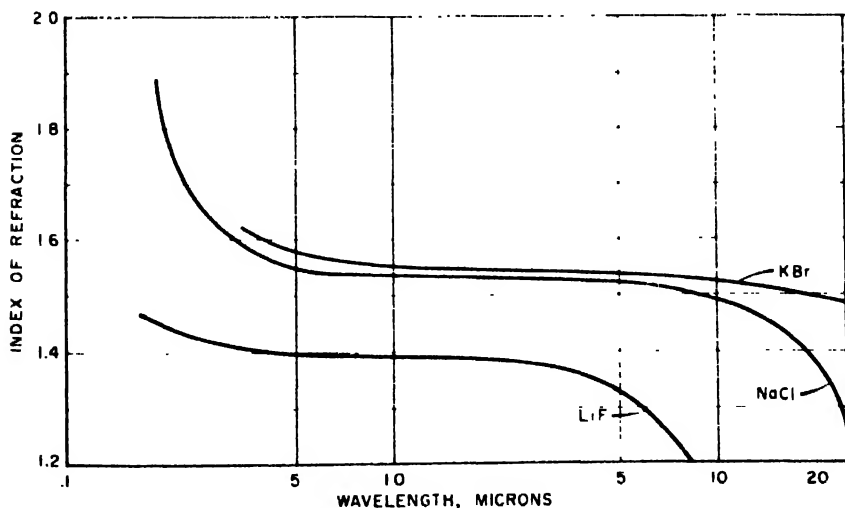


FIGURE 3-2. Index of refraction vs wavelength for some infrared transmitting materials.

this occurs in the region of transmission cut off. Figure 3-2 also shows the increasing index toward short wavelength. The diagram Figure 3-3 traces the dispersion of rays of 3μ and 10μ wavelengths through a 60 degree

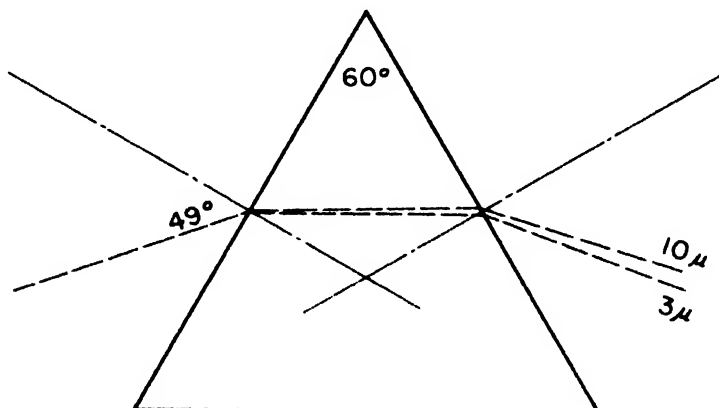


FIGURE 3-3. Ray trace of dispersion of 3μ and 10μ light by a 60° NaCl prism.

rocksalt prism. The single pass results in an angular dispersion of 2.8 degrees between these two wavelengths. In a Littrow monochromator where the beam is reflected back for a second pass through the prism, the total angular dispersion is doubled.

Minimum Deviation. When a prism is installed in a spectrometer it is desirable to have it positioned for minimum deviation which occurs when the light passes through the prism parallel to the base and the angles of incidence and emergence are equal. In this condition the prism aperture is at maximum and dispersion is maximum. With the Littrow mounting one must choose a compromise wavelength for the minimum deviation position since this is a variable depending on refractive index. A good compromise is to choose a wavelength near the middle of the refractive index range covered.

Temperature Effect. For stability of the wavelength calibration of a prism spectrometer it is desirable to thermostat the instrument. An increase in temperature lowers the refractive index of the prism material, giving a smaller deviation and thus shifting the band positions toward longer wavelength readings on the calibration scale. Although commercial spectrometers are usually equipped with a temperature compensating device, this cannot be completely effective because of temperature gradients which develop between different parts of the spectrometer and gradients through the volume of the prism.

Gratings. Suitable gratings for use in the infrared have only recently become available in commercial quantities, as high quality replicas of master rulings. Previously they were made only on an experimental basis at certain universities.

Manufacturing. Rowland at Johns Hopkins University about 1890 was the first to successfully rule a relatively large high quality grating. The work calls for the utmost in skill and patience. As evidence of the precision required we can quote some of the specifications which are met in ruling the best high resolving power gratings. An accuracy of better than 0.01μ is maintained in the spacing of the grooves, requiring temperature control of the ruling engine to better than 0.01°C for the period of days necessary to rule the thousands of grooves on a master grating. Further requirements are for an optical flat surface to better than $\frac{1}{4}$ fringe for the glass backing plate. For high efficiency in the reflectivity of the grating, much care is required in adjusting the ruling diamond so that the grooves have the desired shape.

Diffraction. Figure 3-4 shows a cross-section diagram of an echelette plane diffraction grating. The grooves are formed on an evaporated aluminum coating about 10μ thick, by a polished diamond tool weighted to form the two flat face sides of the grooves. Referring again to Figure 3-4, the width of a groove "a" is the grating constant and is equal to the reciprocal of the grooves per millimeter. This space should not be substantially less than the longest wavelength of the range to be studied. If the wavelength is substantially longer the grating acts chiefly as a mirror, causing a large

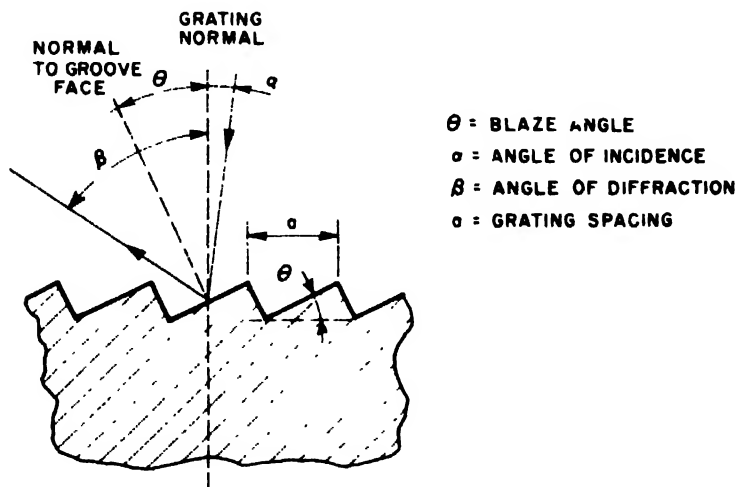


FIGURE 3-4. Diagram of grating surface and principle of diffraction.

portion of the useful light to be directed into the zero order. A grating is usually made with a blaze angle which is determined by using the wavelength in the center of the region of use to calculate the angle of the groove face which will specularly reflect the light at the same angle that light of this wavelength will be diffracted. For the wavelength of the diffracted rays in a particular direction the classical grating equation applies:

$$n\lambda = a(\sin \alpha \pm \sin \beta) \quad (3-5)$$

where n is any integer and denotes the order, a is the groove spacing (grating constant), α is the direction of the collimated incident beam measured from the normal of the grating face and β is the direction of the diffracted wavelength also measured from the normal. Whether $\sin \beta$ is plus or minus depends on whether the incident and diffracted beams are on the same or on opposite sides of the normal. The sign is minus when they are on opposite sides as depicted in Figure 3-4. The equation can be derived from a diagram such as Figure 3-4 by establishing the condition in which the direction of the diffracted beam is such that there is an even number of half wavelengths in the path difference for the rays from two adjacent grooves. This allows that $\lambda \cdot n$ (where n is any integer) will be diffracted in the same direction. This accounts for the origin of the higher orders which must be separated if one is to obtain a pure spectrum with a grating. Two commonly used devices for order separation are a relatively low resolution foreprism spectrometer or long wavelength pass filters to reject short wavelengths. The efficiency of a grating falls off on either side of the blaze wavelength and is usually limited to about a 3:1 wavelength range in the first order. If a wider range of wavelengths is required from a single grating it can be used at higher orders. For example, a 12μ blazed grating is used in the first through the fourth order in a Perkin-Elmer Model 12C and 112 converted to grating use to cover from 2.2 to 18μ in five orders.⁴⁹ The ranges become successively shorter in the higher orders with increasing difficulty of separation and it is usually preferred to limit the grating use to first order only or first and second orders. For examples of commercial spectrometers there is the Perkin-Elmer 237 which uses two gratings in the first order only with a long wave cut on filter program as follows:

Grating #1

2.5 to 8μ (1st order) (4000 to 1250 cm^{-1})

Filter #1 2.5 to 4.2μ

Filter #2 4.2 to 8.0μ

Grating #2

5 to 16μ (1st order) (2000 to 625 cm^{-1})

Filter #3 5μ (2000 cm^{-1}) to 8.4μ

Filter #4 8.4 to 16μ

An example of a fore-prism grating spectrometer is the Beckman IR-9 using two gratings both in first and second orders as follows:

- Grating #1 2.5μ (4000 cm^{-1}) to 5μ (2000 cm^{-1}) 2nd order
- Grating #1 5μ (2000 cm^{-1}) to 8.3μ (1200 cm^{-1}) 1st order
- Grating #2 8.3μ (1200 cm^{-1}) to 15μ (666.7 cm^{-1}) 2nd order
- Grating #2 15μ (666.7 cm^{-1}) to 25μ (400 cm^{-1}) 1st order

Comparison of Prism and Grating. The dispersions of a typical grating and rock salt prism are compared in Figure 3-5. These curves illustrate the consistently high and relatively constant dispersion of the grating while the

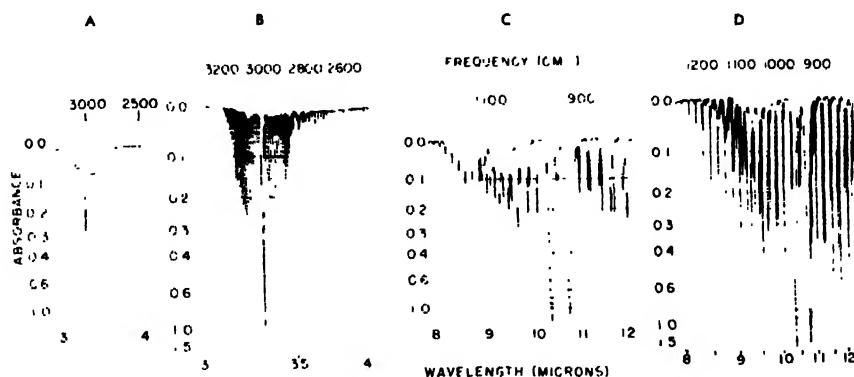


FIGURE 3-5. Comparison of portions of the spectra of two light gases by grating and rock salt prism spectrometer. (A and C) Methane and ammonia respectively with rock salt prism. (B and D) Same with grating. Signal-to-noise is 400-1 for the prism and 600-1 for the grating.

prism suffers in the comparison, especially in the short wavelength portion of the range, but it improves to a peak at its long wavelength transmission limit.

The dispersion advantage of the grating can be used in a number of ways to improve spectrometer performance. For use in chemical analysis, maximum resolution is often of secondary importance and therefore wider slits would be used. Typically one might use a slit program giving a factor of two improvement in signal-to-noise as compared to the prism still leaving a resolution advantage ranging from 6 to 3 for the grating. An additional benefit of the grating's higher dispersion will be realized in the precision of measuring the wavelengths of points in spectra. The grating wavelength calibration is less sensitive to temperature by approximately three times the dispersion ratio. The three comes from the ratio of the linear to cubic expansion coefficients. The effects of any deficiencies in the precision of the scanning mechanism are also reduced by the dispersion ratio.

Theoretical Resolution Limit. One should be aware that even with a perfect optical system in perfect alignment, any given prism or grating has a certain theoretical resolution limit as a result of the diffraction pattern of the horizontal aperture of the monochromator system. This limitation may become more significant in the future, if as expected, the use of cooled detectors becomes prevalent. Spectroscopic resolving power is defined as the ratio of the average wavelength of two very narrow neighboring spectral lines or absorption bands, to the minimum separation $\delta\lambda$ for detecting that the two lines form a doublet. Rayleigh has suggested, and it is generally accepted, that $\delta\lambda$ for the theoretical limit of resolution of the system is the condition when, with an infinitely narrow entrance slit and monochromatic lines, the angular dispersion between the two lines is equal to the angular separation between the central maximum and the first minimum in the diffraction image of one line. The diagram of Figure 3-6 will serve as an aid to illustrate the method of calculation of the diffraction limit. The width of the beam at the collimator which will just fill out the prism or

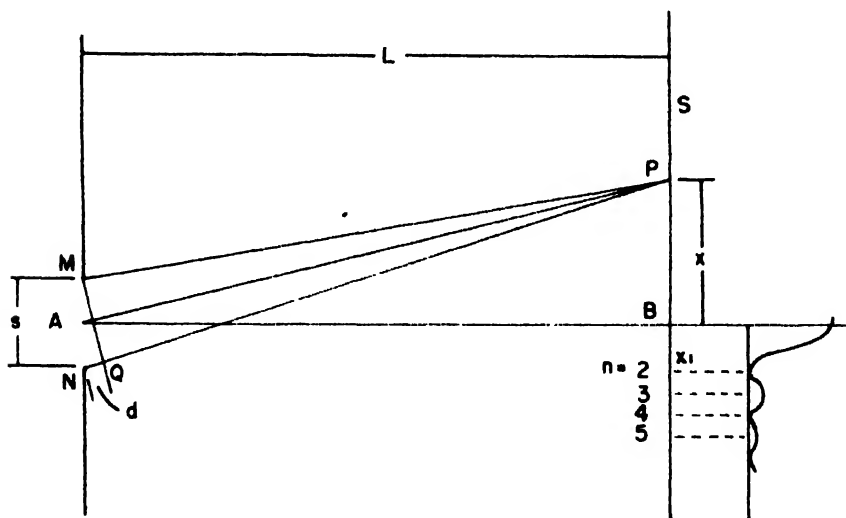


FIGURE 3-6. Diagram illustrating the origin of diffraction limit of resolution of a monochromator.

grating is represented by s with the focal plane S of the exit slit at distance L from the aperture MN . The line AB is drawn perpendicular to the middle of the aperture MN from the plane S . P is a point in the plane distance X from B . MQ is drawn at right angles to AP so that NQ or d is the difference in path length of the extreme rays NP and MP . If $d = \lambda$ (one wavelength),

P will be a point of darkness. To prove this we can take the two halves of the aperture MA and AN and match each point in one half with a corresponding point on the other half for which the path difference is $\lambda/2$. Consequently, the light from the entire upper half annuls that from the entire lower half. For a point farther along S from B for which $d = \frac{3\lambda}{2}$, the slit may be regarded as composed of three sections, two of which will annul each other while the remaining section will illuminate the point at $\frac{1}{4}$ intensity. A general expression for the diffraction pattern for the system diagrammed is: $x = \frac{n\lambda L}{2S}$ with minima occurring when $n =$ an even integer (2, 4, 6 ...) and maxima occurring when $n =$ an odd integer (3, 5, 7 ...). The relative intensities at different points are indicated by the curve in the lower part of the figure. The angular separation of the central maximum and first minimum is x_1/L . From the dispersion of the grating or prism we can calculate the wavelength separation $\delta\lambda$, which then by definition is the theoretical resolving power.

Detectors and Detector Optics

In the foregoing, the various components of an infrared spectrometer have been discussed somewhat in the order of the path of the light through the instrument. It will now be assumed that there is a narrow wavelength interval of light passing through the exit slit which is to be detected.

Photo Detectors. The type of detector chosen will depend on several considerations, but first of all on the wavelength range to be studied. Wavelength is important because the effect that a photon can produce on a detector depends on its energy which, according to Planck's theory: $E = h\nu$, where ν is the frequency of the radiation and $\nu = c/\lambda$. For the longer wavelength infrared the photon energy is very low (about 0.03 eV at 40μ) so that these energies are masked by the thermal energy of the material at room temperature and cooling is required for effective operation. Photo conducting detectors using doped germanium can be made for wavelengths to 130μ (77 cm^{-1}) where the photon energy is about 0.01 eV. They must be operated at liquid helium temperature and are considered uneconomical for the average user. Progress is being made in the development of closed system, helium refrigerators and it can be assumed that in the future a helium-cooled detector will be standard for the better infrared spectrometers. This does not necessarily mean with a photo-conductive type detector, but it may be a thermal type for which performance can also be much improved by cooling.

Thermal Detectors. For a wide range detector, at present one of the thermal types would be a logical choice. This class makes use of an ab-

sorbing receiver to convert the radiant energy to heat. The actual detection then requires a sensitive means of measuring small temperature changes. The three types of thermal detectors in common use are the radiation thermocouple, bolometer and pneumatic detector. Since all modern infrared spectrometers use either flickered or interrupted radiation at frequencies in the six to thirty cycle range, a further requirement is that the response time be short enough to give good sensitivity at these frequencies. For thermal detectors this requires that the total mass represented by the receiver, the absorbing material, and temperature sensing element will heat or cool during $\frac{1}{2}$ cycle of the chopping frequency. A detailed presentation of the theory of thermal detectors is not regarded to be within the scope of this chapter, so we will refer to some excellent theoretical design papers which have appeared in the literature^{2,9,10,15,30,35,61,64} and the discussion here will be confined to the principles of interest from a user's point of view.

Radiation Thermocouple. Because of their simplicity of operation and availability, radiation thermocouples are at present the most popular type of wide range detector. One method of construction is illustrated in Figure 3-7. T is the target or receiver. Its size is chosen to match a reduced image of the exit slit of the spectrometer. The target is usually made of gold foil

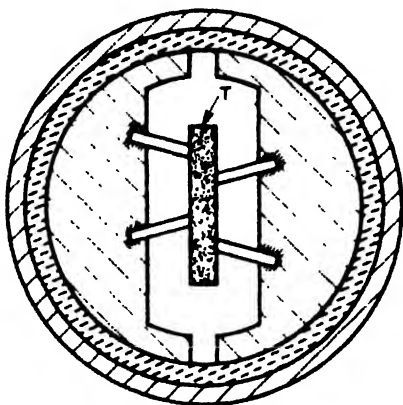


FIGURE 3-7.
Radiation thermocouple.

and is coated with an infrared absorbing material. The blackening may be accomplished by evaporating gold onto the target in an atmosphere of a few millimeters of hydrogen. This causes the gold to deposit in a black fluffy layer like soot and is quite effective in trapping the incident radiation and converting it to produce a temperature elevation of the receiver. To the receiver may be welded two or four short fine wires in pairs of dissimilar metals, forming the hot junctions of the couples while the outer ends of the leads are attached to heavy metal lugs which act as heat sinks for the

cold junctions. The response of the thermocouple to radiation is analogous to an electrical current flow in a resistive circuit where the radiation falling on the receiver (represented by the current) develops a thermal potential (ΔT) across the thermal impedance between the hot and cold junctions. The thermal impedance of a radiation thermocouple is comprised of three components: (1) heat lost by radiation from the receiver, (2) heat lost by conduction of any residual gas in the enclosure, and (3) heat conducted by the thermal junction wire leads. Since the detector will generally be used in an interrupted light system, its time constant is of interest and we can carry the electrical analog further by comparing the heat capacity of the receiver and junctions to electrical capacity and the time to reach thermal equilibrium is proportional to the product of thermal capacity and thermal impedance. The signal voltage developed in the average spectrometer using a thermocouple detector may be of the order of 0.1 to 2.0 microvolts in about ten ohms resistance. With the availability of fast response thermocouples, galvanometers and current breaker amplifiers have been completely abandoned. The pulsed voltage developed by radiation chopping is suitable for transformer coupling to match the input impedance of electronic tube amplifiers. With a well designed system it is possible to reach the signal-to-noise limit imposed by the Johnson³⁷ noise of the thermocouple resistance at room temperature.

Bolometer. The bolometer, like the thermocouple, is also a device for detecting the heating produced by absorbed infrared radiation. It is usually made of a ribbon of metal or semiconductor flake chosen for a high temperature coefficient of resistivity. The strip is supplied with a virtually constant current through a load resistor which, for good efficiency, should have at least ten times the resistance of the sensitive element. The bolometer excitation is usually DC but AC systems have been used successfully. In either case the excitation current or voltage needs to be kept out of the input to the amplifier, either by a balanced bridge arrangement or, in the case of a DC system, a blocking capacitor may be used. Both arrangements are illustrated in the diagrams of Figure 3-8. In circuit A the values of components in the bridge are selected for near optimum conditions of sensitivity of the bolometer, maximum transfer of the signal generated into the transformer, and for minimizing the sources of Johnson noise in the transformer primary. This requires a high ratio of load resistance to bolometer resistance and a low ratio of balancing leg resistance to bolometer resistance. One frequently sees a treatment of Wheatstone bridge theory which proves that for maximum transfer of power into the measuring device, the bridge should have four equal arms. It should be recalled, however, that the conditions established for this analysis set a limit on the voltage available for bridge excitation and set no excitation current limit on any

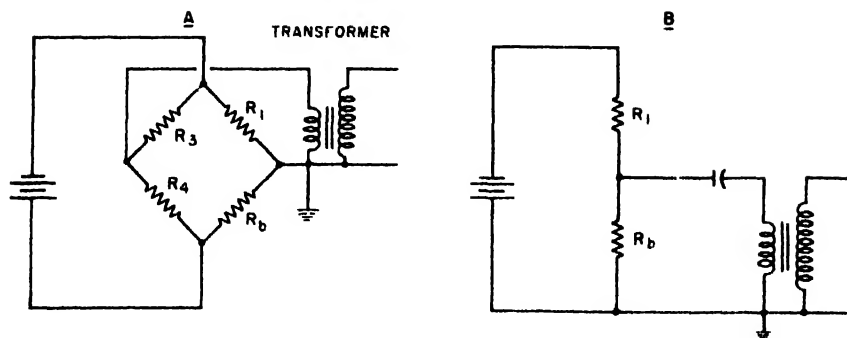


FIGURE 3-8. Metal bolometer circuits.

of the bridge arms. In designing a bridge for a bolometer the starting point is the optimum excitation current which would be determined empirically in consideration of signal-to-noise. From this point we can assume that excitation current and voltage are cheap and there will be no limits set. The next step is to choose the load resistor R_1 . The expression for the voltage across the bolometer is:

$$E_b \approx R_b I_1 \quad (3-6)$$

where

$$I_1 = \frac{E_r}{R_1 + R_b}$$

Then

$$E_b = R_b \frac{E_r}{R_1 + R_b} = \frac{E_r}{\frac{R_1}{R_b} + 1} \quad (3-7)$$

The efficiency of this part of the circuit can be expressed as the ratio of a change in E_b (ΔE_b) to a change in R_b (ΔR_b) or $\text{Eff} = \frac{\Delta E_b}{\Delta R_b}$. By substituting values in the above expression it will be seen that the ratio is near optimum of over 90% if the ratio of R_1 to R_b is > 20 . The excitation voltage is then chosen to produce the optimum bolometer excitation current in the series combination of $R_1 + R_b$. Since R_4 is in series with R_b and the transformer primary where it is a source of Johnson noise and also an attenuating resistance in the signal circuit, it is desirable to make its value small compared to R_b . Again a ratio of 10 or 20 is near optimum. The final selection then is to adjust R_3 to balance the bridge. To avoid current noise in this system good solid connections and wire-wound resistors are required as well as a conservatively rated, extremely steady current source, such as a storage battery.

In circuit B, R_1 is selected again using the same considerations discussed above in regard to the bridge circuit. C must be chosen to provide low impedance compared to the bolometer and transformer primary at the low chopping frequency. This results in a capacitor value of the order of $1000\mu\text{f}$ for metal strip bolometers. Electrolytic capacitors are usually not well suited for this purpose because they frequently contribute an additional noise component. For low impedance bolometers the bridge circuit A would be favored to avoid the large size of about $1000\mu\text{f}$ oil filled paper capacitor.

Bolometers made of thermistor material (a combination of the oxides of nickel, manganese and cobalt) have been described by E. M. Wormser⁶⁸ and by W. H. Brattain and J. A. Becker.⁸ This material has a high negative temperature coefficient and high resistivity. Because of the difficulty of constructing and mounting a suspended flake thin enough for rapid response, the sensitive element is fabricated about 10μ thick and supported on a glass or quartz backing plate. This increases the heat conductivity from the strip to give a more rapid response time at a sacrifice of sensitivity.

The high temperature coefficient of resistivity compensates in part for the comparatively high heat conductivity. This results in a detector with performance approximately equivalent to metal strip bolometers.

Dielectric Bolometer. It has been proposed to make use of the high temperature coefficient of dielectric constant of certain materials (for example, barium and strontium titanates), and the preliminary investigations look very promising.²⁷ Hanel indicates that this type of detector could be made temperature-limited but apparently as yet very little experimental work has been done with it.

Because there is inherently a loss in detectivity when a given quantity of radiation is spread over a larger area, a bolometer is frequently used as the detector in larger spectrometers. In the case of a bolometer, part of the loss can be recovered by optimizing the excitation voltage for the larger area.

Cooled Detectors. An ideal thermal detector should be limited in detectivity by the temperature fluctuations in the detector. In general, room temperature thermal detectors are Johnson noise limited, which is about a factor of ten greater than the limit set by temperature fluctuations in the detector. This points to the direction from which improved performance of thermal detectors might be obtained. For example, if materials could be found having a greater temperature coefficient of resistivity for bolometers or higher thermo-electric power for thermocouples, improved performance would result because these factors would not in themselves affect Johnson noise. Yet the signal response for a given ΔT would be increased. Johnson noise can also be reduced by cooling the detector. Improved

performance would result provided the materials would retain their sensitivity to temperature changes at the new temperature.

Several workers have successfully attained marked gains in detectivity, especially with bolometers, by cooling the detector but none of the systems are in general use yet. Some have taken advantage of the unusually high temperature coefficient of resistivity in the transition region to superconductivity of certain materials. Although some very sensitive measurements have been made using this technique, the difficulties of continuous stable temperature control in the narrow transition region are severe enough to discourage widespread acceptance of this type of detector.

A detector was described by Rodgers and Boyle.⁵⁶ They used a flake of carbon resistor material cooled to 2°K where the material has a high α and low specific heat. Without adding any specific blackening to the surface, the material has good absorptivity even in the far infrared.

Texas Instruments at their Houston research laboratories are developing a bolometer which uses the high temperature coefficient of resistivity of gallium-doped germanium at around 4°K. Typical performance capabilities quoted for this detector are NEP of 10^{-12} watts using a 2 by 2 mm receiving area, 35 cps chopping speed, and a background limiting cone angle of 12°.

The liquid helium-cooled detectors perform best when used with cold aperture stops and cold filters so that the amount of room temperature background radiation reaching the detector is minimized. In the interest of sensitivity the conductivity to the cold work-surface must be low. Then if the background radiation from a wide angle is allowed to reach the detector, its temperature will be elevated out of the sensitive region. These helium-cooled bolometers offer a theoretical, and sometimes actually attained, advantage of a factor of about 100 in signal-to-noise over room temperature thermal detectors. But with the difficulties and high cost of operation, a less ambitious approach may be a good compromise for the average user. Nickel ribbon bolometers have been operated at liquid nitrogen temperature. Malnev and Kremenchugski report a gain of 15 to 20 for this type of operation.⁴² It appears that their comparison is with an unevacuated room temperature bolometer. One can expect a gain of four to five by evacuation alone so the gain from cooling may be only about four. This would be a valuable improvement in spectrometer performance which should be economically justified at the relatively low cost of liquid nitrogen.

Pneumatic Detector. One form of the pneumatic detector is commonly used in continuous stream gas analyzers. It is a cell filled with a specific gas, making it sensitive to radiation of certain wavelengths only. Interrupted radiation causes cyclical heating and cooling of the gas and the resulting pressure changes are detected by detecting the movement of a thin diaphragm built in as one wall of the cell.

For use in scanning infrared instruments, M. Golay has described a pneumatic detector which has uniform absorptivity for radiation from the ultraviolet to microwaves.²²

In this detector the absorptivity does not depend on the usual black, fluffy coating but rather is accomplished in the metallized plastic film (Figure 3-9). The film is coated with evaporated metal to have a resistivity of about 300 ohms per square which causes the film to offer an impedance

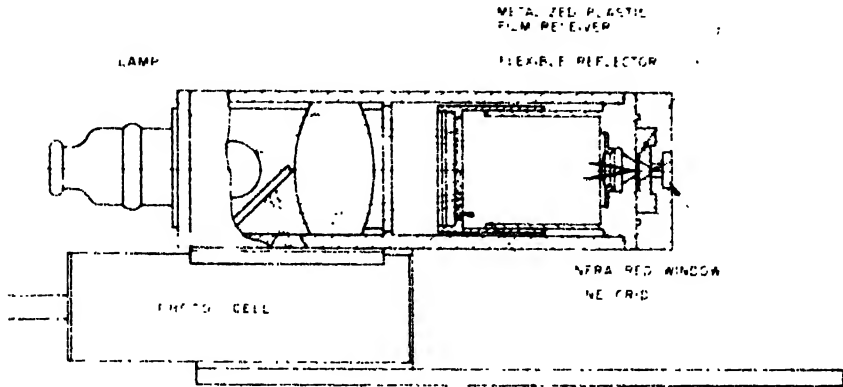


FIGURE 3-9. Golay pneumatic detector.

to an electromagnetic wave with the result that the absorbance is independent of wavelength so long as the wavelength is small relative to the area of the film.

In regions of the spectrum where thermocouples and bolometers can be made with good absorptivity of the receiving surface, their performance is approximately equivalent to that of the pneumatic type. The Golay detector is usually used for the far infrared beyond 50 or 100 μ because of its uniform absorptivity and its wide receiving area. The latter is desirable in the far infrared because of the wide slits required.

Detector Comparisons. Table 3-2 lists some detectors and comparative data on their design and performance characteristics. For those column headings which may not be self explanatory, we give the following definitions:

(1) **Responsivity** -- the terminal voltage output per watts of incident radiation falling on the detector. (We are, of course, generally dealing with microwatts and microvolts and the linear range need extend only over a range of up to a few microwatts.)

(2) **NEP** -- this refers to the noise equivalent power, which is a measure of the sensitivity. It is defined as the amount of radiant power which, when

TABLE 3-2.

Detector	Responsivity (volts/watt)	NEP (watts)	Detectivity, D^* (cm ² /watt)	Temperature (°K)
Thermocouple (Reeder)	5-15	4×10^{-11}	1.6×10^9	300
Golay Cell (Eppley)		8×10^{-11}	4.2×10^9	300
Platinum Bolometer	20	4×10^{-11}	3.5×10^9	300
Ge Bolometer		1×10^{-12}	2×10^{11}	4.2 K
GE : Zn Photocond			1×10^{10}	4.2°K

falling on the detector, will produce an rms electrical signal equal to the rms noise signal inherent in the detector. The units are in watts and unless otherwise defined, it is generally assumed to refer to the noise in a one cycle per second band-width measuring system. Noise equivalent power can be determined from the noise figure and responsivity data by the relation:

$$\text{NEP (watts)} = \frac{\text{noise (volts)}}{\text{responsivity}} \text{ volts/watt} \quad (3-8)$$

For an example, we will calculate the NEP for a ten ohm thermocouple detector at room temperature with Johnson noise as the dominant noise source. The responsivity of the detector is given as ten microvolts per microwatt. First, it will be necessary to calculate the Johnson noise for the given conditions in a one cycle bandpass according to the formula:

$$V_j = (4KTR/f)^{1/2} \text{ volts} \quad (3-9)$$

where K is Boltzmann's constant.

At room temperature for a one cycle bandpass this reduces to:

$$V_j = 1.3 \times 10^{-10} R^{1/2} \text{ volt.} \quad (3-10)$$

For 10 ohms then $V_j = 1.3 \times 10^{-10} \times 10^{1/2} = 4.1 \times 10^{-10} \text{ volt.}$

$$\text{NEP} = \frac{V_j}{\text{Responsivity}} = \frac{4.1 \times 10^{-10} \text{ volts}}{10 \text{ volts/watt}} = 4.1 \times 10^{-11} \text{ watt} \quad (3-11)$$

Since there is a dependence of the minimum detectable power on A , the area of the receiver (the heat loss by radiation from the receiver is proportional to A), Jones has introduced a term "detectivity," designated D^* , which is commonly used to describe detector performance. It is related to NEP and A :

$$D^* = \frac{\sqrt{A\Delta f}}{\text{NEP}} \text{ cm}^2/\text{watt} \quad (3-12)$$

Detector Optics. In a spectrometer application the radiation to be detected emerges from the exit slit and the area is outlined by the slit. The detector size is determined by the maximum slit opening and the optics. It has been shown that heat lost by radiation from a detector is reduced by reducing the receiver area. Therefore, a minimum size detector is desirable. It is the purpose of the optics to focus the exit beam onto the detector as a reduced image of the exit slit with the greatest reduction ratio obtainable. An ellipsoidal mirror is generally used because it avoids spherical aberrations and any light originating at the point of one focus and reflected from the ellipsoidal surface, will pass through the other focus. Any given ellipsoidal mirror then can be used at only one ratio of image reduction because the image definition rapidly deteriorates if the mirror position is altered from that at which the slit is located at one of the foci. Since the slit acts as an extended source in one direction at least, the ends of the slit are off the axis of the ellipse. This gives rise to an aberration called coma where the ends of the slit image flare out into a sort of "bow tie" effect. The effect becomes more serious the higher the ratio of reduction. The actual reduction ratio chosen must be a compromise to limit aberrations and reflection losses at the detector and detector window.

The reduction ratio is further influenced by the angle of divergence of the light beam from the exit slit or its equivalent, the f number of the spectrometer.

The diagram of Figure 3-10 is included to illustrate these relations. We will assign (somewhat arbitrarily) 90 degrees as the maximum angle of con-

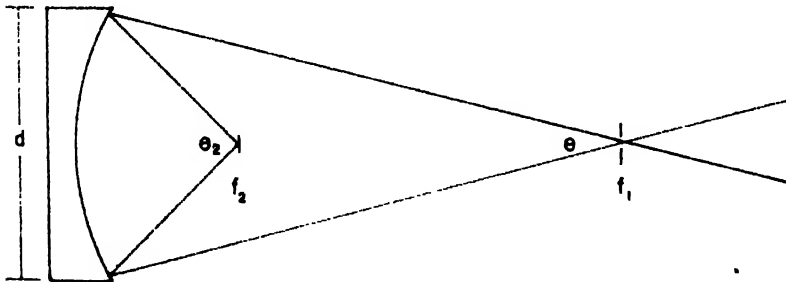


FIGURE 3-10. Diagram to illustrate the relation of monochromator aperture and maximum ratio of image reduction of detector optics.

vergence on the detector window. (From the diagram it seems apparent that this is not far from a reasonable assumption.) If $\theta_2 = 90$, then $f_2 = d/2$. To a near approximation

$$f_1 = \frac{d}{\sin \theta}$$

The ratio of image reduction is

$$M = \frac{f_1}{f_2}$$

Then

$$M = \frac{d \sin \theta}{d/2} = \frac{2}{\sin \theta}$$

For an $f/4$ monochromator this calculation results in a ratio of 8 to 1 for the maximum reduction ratio.

Sometimes the flat detector window is replaced with a convex spherical lens to provide some additional image reduction.

Infrared Optical Materials

Alkali Halides. The list of optical materials available for transmission in the infrared continues to grow. First it was discovered that alkali halide crystals had transmission ranges beyond that of glass and quartz and were extremely useful for cell windows and refracting elements. The natural crystals were sought for this purpose but their limitations were in size, clarity and the presence of impurities which cause undesirable bands. Later the technique of growing large pure single crystals synthetically was developed and the list is now essentially complete from LiF to CsI. These materials are listed in Table 3-3 with their long wavelength transmission

TABLE 3-3. LONGWAVE LIMIT (60% T FOR 1 cm)

Material	Microns
LiF	6.2
CaF ₂	9.
NaF	10.5
BaF ₂	11.5
NaCl	16
KCl	20
KBr	25
CsBr	38
CsI	50

limits. The limit is here defined as 60% transmission for a 1 cm thickness. The obvious relation between the atomic weight of the elements in the crystal and the long wavelength cut-off should be noted. Only a few of these materials have substantial resistance to fogging and erosion by moisture. These are principally the fluorides and the most commonly used are LiF, CaF₂ and BaF₂. Many applications require a longer transmission range than these afford and developments to extend the range of water-resistant materials has continued.

Other Materials. Table 3-4 lists some materials not included in Table 3-3, available for infrared windows and essentially unaffected by water. The Irtran series of Eastman Kodak and T-12 of Harshaw are pressed polycrystalline materials and have greater resistance to thermal shock than the single crystal form. The long-wavelength limits are approximate calcula-

TABLE 3-4. LONGWAVE LIMIT (60% T FOR 1 cm)

Material	Microns
Glass	2.7
Quartz SiO_2	3.6
Sapphire Al_2O_3	5.9
Periclase MgO	7.8
Servofax As_2S_3	8.4
Harshaw T-12	10.0
Irtran I	6.4
Irtran II	10.5
Irtran III	8.7
Irtran IV	15.5
Irtran V	6.0
Silver chloride	14.5
KRS-5	40.0
Diamond	none

tions from transmission curves of other thicknesses. The wavelengths quoted are again, as in Table 3-3, the 60% transmission points for a 1 cm thickness.

As a source of engineering information on other physical properties of most of these materials, the following is recommended: Jamieson, J. A., McFee, R. H., Plass, G. N., Grube, R. H., and Richards, R. G., "Infrared Physics and Engineering," Chapter 7, New York, McGraw-Hill Publishing Co., Inc., 1963.

PRACTICAL SPECTROMETERS

Popular Monochromator Systems

Off-axis Parabola. The diagram of Figure 3-11A illustrates the arrangement and optical path of a basic single-beam prism monochromator with an off-axis parabolic collimator. This is the Littrow arrangement which is characterized by the plane reflecting surface M_4 behind the prism to return the collimated beam through the prism a second time for twice the dispersion of a single pass. A variation of this is the Walsh double-pass monochromator system (Figure 3-11B) which contains the additional mirrors M_8 and M_9 and the internal chopper C_2 . These components intercept the first pass through the monochromator, modulate it at the interruption fre-

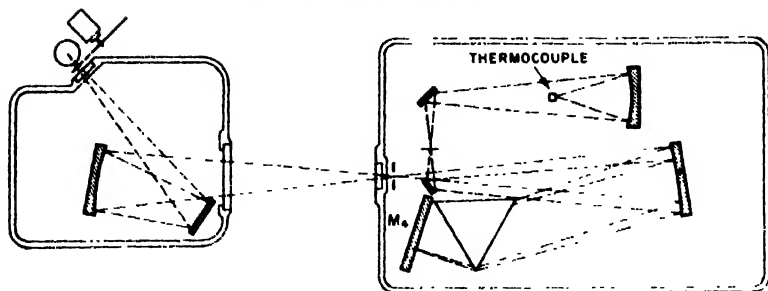


FIGURE 3-11A. Littrow-prism monochromator with off-axis parabolic collimator.

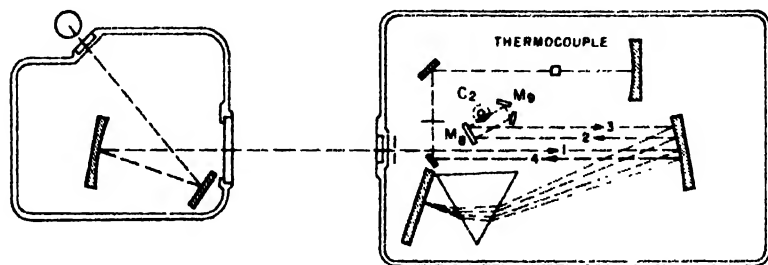


FIGURE 3-11B. Littrow-prism monochromator with the Walsh double-pass system.

quency and return it for a second pass, giving a total of four passes through the prism. The mirror M_9 is a corner reflector required to transpose the spectrum into the required sequence so that dispersion will be additive. A portion of the first pass spectrum of a different wavelength will be falling on the detector simultaneously with the second pass but the amplifying system only responds to the modulated second pass spectrum.

The off-axis parabola is capable of high performance, provided the mirror's figure is very accurate. To understand the operation of an off-axis paraboloid it is convenient to consider it as a section cut from the side of a paraboloid somewhat larger than twice the diameter of the section. The entrance and exit slits are located optically as close together as possible on the axis of the imaginary large mirror with the collimated beam directed parallel to the axis. The angle of off-axis use is the angle between the reflected collimated beam and the center ray of the incident beam from the slit. For a sharp focus the adjustment of the angle of use is quite critical that it conform to the angle for which the mirror was made.

In Figure 3-11A we will note that the beam from the entrance slit is offset from the center of the collimator on the side away from the exit beam. This allows the dispersed beam returning from the prism to fall fully on the collimator, but offset the same amount on the opposite side

of center, from whence the dispersing spectrum is focused on the plane of the exit slit.

This same arrangement can be used with a grating by mounting the grating at the Littrow mirror position and removing the prism. The collimator also would need to be replaced with one figured at a different off-axis angle.

Czerny-Turner and Ebert. Figure 3-12 is a diagram of another popular monochromator arrangement. It uses a grating dispersing element for which it is especially well suited because of the symmetry. The Littrow prism arrangement is also adaptable. This is the Czerny-Turner and it is

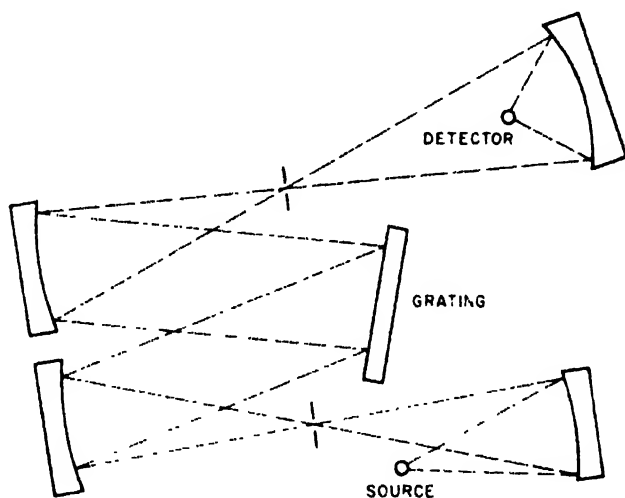


FIGURE 3-12. Czerny-Turner type grating monochromator.

characterized by two collimators. One receives the incident beam from the entrance slit and reflects the collimated beam to the dispersing element. The other receives the return dispersed beam and focuses the spectrum at the exit slit. The arrangement is such that off-axis aberrations are compensated and sharp images are formed, requiring the use of only good quality spherical mirrors which can be obtained at far less cost than one good off-axis paraboloid.

The above system is sometimes inaccurately referred to as the Ebert system which is quite similar but is distinguished by having one large spherical mirror similarly mounted instead of the two smaller collimators.

Prism-grating Monochromator. As we have seen in a foregoing section, grating spectrometers require a method of separating the orders of the spectrum. This has been done since some of the earliest grating spec-

trometers with a fore-prism monochromator. Figure 3-13 is a diagram of the Beckman IR 9, a typical instrument of this type. If the grating use is confined to lower orders such as the first and second, the resolution of the

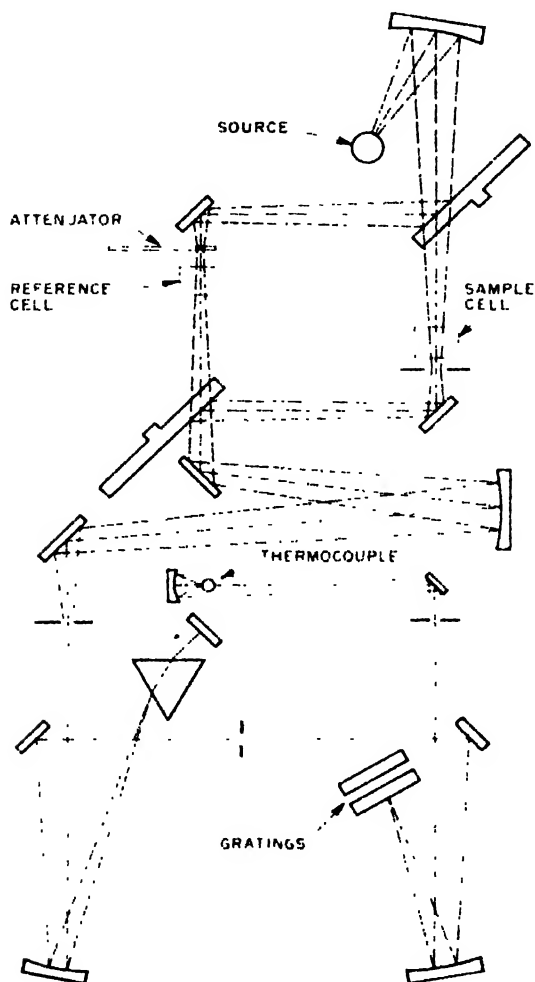


FIGURE 3-13. Prism-grating optical-null type spectrophotometer (Beckman IR 9).

prism monochromator can be quite low, because it need only exclude the adjacent orders, but for the higher orders, the interval gets successively narrower. This is shown in Table 3-5. If this grating were to be used in the fifth order, the sixth which is only 0.4 microns away, would need to be separated in a region where the prism material would have low dispersion.

TABLE 3-5. ORDER WAVELENGTH

1st	12 μ
2nd	6
3rd	4
4th	3
5th	2.4
6th	2.0

The slit width of the prism monochromator also must be maintained wide enough to fill out the widest slits of the grating monochromator. For a wide range instrument, therefore, it is preferable to use several gratings to confine the use to lower orders.

Filter-grating Monochromator. A second means of order separation for grating monochromators was described by Gaunt.¹⁷ The success of this instrument was severely limited by the performance of the filters. He used F-centered alkali halide crystals which did not provide the desired steep cut on slope and high transmission in the region of use, especially at longer wavelengths.

More recently with the advances in the development of multi-layer interference filters, a highly successful line of filter-grating spectrometers has been developed. One was first described by Alpert in 1962.¹ This type of grating spectrometer is now also included in the Beckman line³⁸ and the range has been extended to 300 μ in the IR-11 model.³⁹ The long wavelength range of interference filters is complicated by the scarcity of suitable transmitting materials for the substrate and interfering layers.

The optical arrangement for a filter-grating spectrometer would be similar to Figure 3-11A or 3-12 with the filters inserted near a slit or slit image where the required size of the filter is not excessive.

Photometry Systems

The monochromators discussed above, except the Beckman IR-9, were shown with a single sample position from the source to the entrance slit. A recorded scanned spectrum from this type of instrument would show relative energy reaching the detector vs wavelength. The energy reaching the detector is dependent upon the spectral radiation pattern of the infrared source, the transmission of the atmosphere in any air paths, the monochromator slit width, any variations of monochromator transmission efficiency with wavelength (for example, prism transmission and grating angle off the blaze), and detector sensitivity variations with wavelength. The absorption spectrum of the sample can be determined from these data by comparing scans made with the sample in the path and sample out, but this can be quite tedious.

Optical Null. To facilitate acquiring the desired data of per cent sample transmission vs wavelength, the concept of automatic per cent transmission recording, using the optical-null principle for infrared spectrometers, was introduced in 1942 and several partially successful systems were developed.^{17,24,26,44,62,65,69} A practical operational system was described in 1947⁶⁹ and an improved version in 1958.³⁴ This system has received wide acceptance and most of the principal manufacturers are marketing a version of it. Some of these are shown schematically in Figures 3-14. They

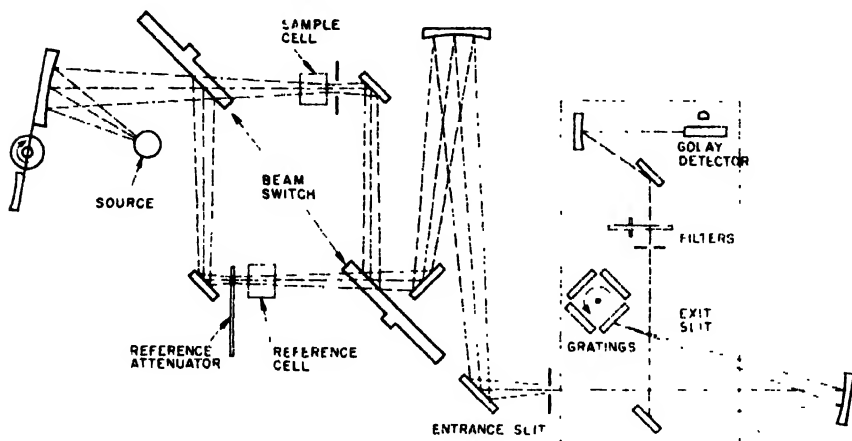


FIGURE 3-14. Commercial optical-null type spectrophotometers.
(A) Beckman IR-11.

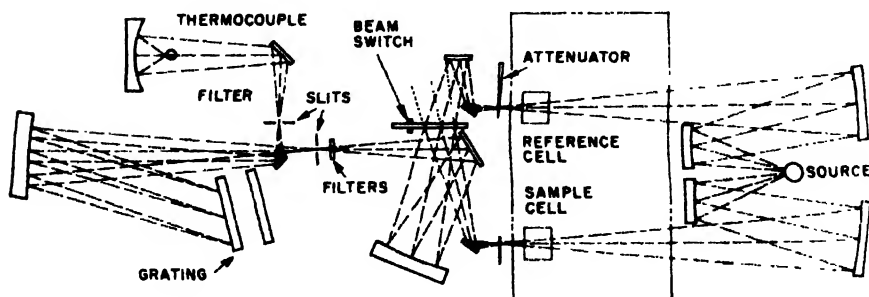


FIGURE 3-14B. Perkin-Elmer 421.

all have in common a double path of source illumination of the monochromator entrance slit with a rotating mirror means of flickering alternately between the reference and sample paths. The detector responds

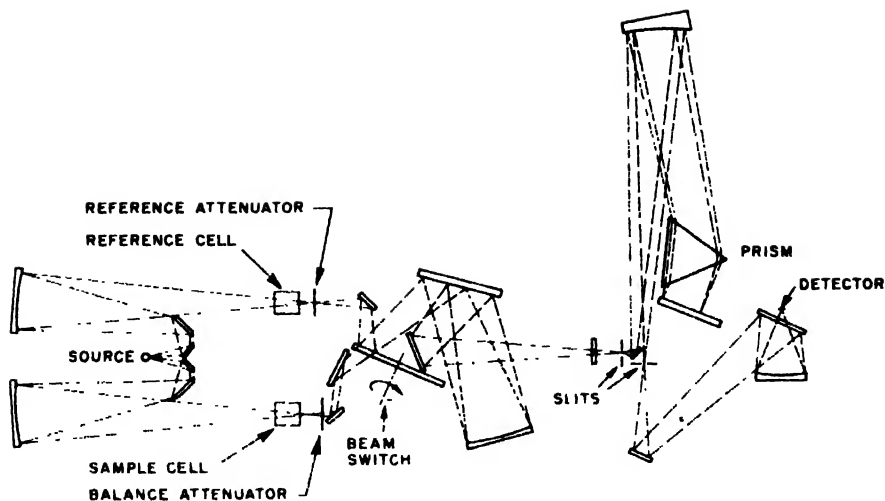


FIGURE 3-14C. Unicam SP-200.

only when the intensity of the two beams is unequal. The recording system responds to any unbalance by causing a light attenuator to move in or out of the reference beam to restore balance. The recording pen is coupled to the light attenuator so that it records the attenuator position as an indication of the sample per cent transmission. Figure 3-15 is a block diagram showing the relation between the parts of an optical-null spectrometer.

The optical-null system, because it is the best available at present, is very popular but it does have at least three quite serious faults which limit the accuracy of absorptivity measurements. First, there is the matter of going dead at zero transmission of the sample. At such times the reference beam attenuator will move in to stop all light in the reference beam. Then there is no light in either beam and the system is completely dead and unable to make a precise measurement. Most attenuators are quite non-linear in the zero to around 3% transmission range, increasing the errors of measurements in this region. Some of the means proposed to obtain acceptable performance are: mechanical stops, upscale drift adjustment and avoiding measurements at low transmission. None of these meet the needs of the critical spectroscopists. The light-by-pass system described³⁴ does meet the requirements for a true live zero balance. In this system about 3% of the reference beam is taken out ahead of the attenuator and added to the sample beam during the sample beam portion of the beam flickering cycle. In regions of opaque sample, the reference attenuator must stay open the approximately 3% required to balance the by-passed portion which is in

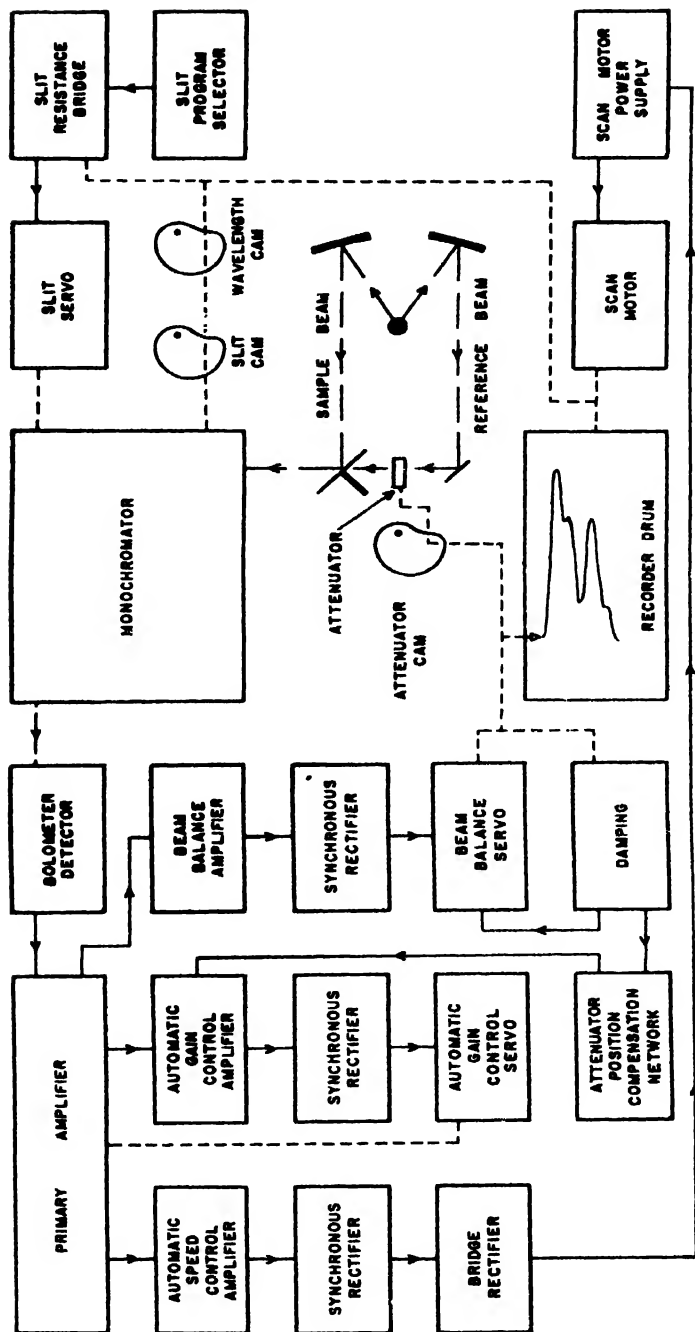


FIGURE 3-15. Block diagram illustrating the interrelation of functions in an optical-null spectrophotometer.

phase with the sample beam. The zero is determined in a dynamic balance condition and is independent of reference beam energy and atmospheric absorption. A further advantage is that since the reference attenuator never closes beyond about 3%, the non-linear low transmission portion of its range is avoided. This feature is not as yet available on any commercial spectrometers.

A second fault of the optical-null system is that because of the necessity of the chopper being located between the sample and the monochromator, any radiation from the sample is also modulated. In the case of warm samples this can contribute a signal which deviates the true balance point in regard to the transmission of light from the source. For example, the zero transmission reading of a polystyrene film at 14.3μ (700 cm^{-1}) may read 1% higher than a 0% transmitting liquid sample at this wavelength. This is because the film temperature quickly rises as a result of the absorbed source radiation while the liquid sample will warm slowly because of the comparatively large mass of the cell windows. This effect is increasingly noticeable toward the longer wavelengths because of the relatively higher temperature of the source, compared to the sample. The power emitted from the sample becomes a larger fraction of the source emission at long wavelength (See Figure 3-1). With high temperature samples such as may be required for fusion, this effect can cause a quite large deviation in the transmission balance point.

The third fault of the optical-null system relates to variations in the measurement of absorbance of a given sample when the series of measurements are made over an extended period of time. The reasons for the deviations have not been completely determined but there is some evidence that the control function of the reference beam attenuator is variable.

Electrical Ratioing. At present there is much interest in electrical beam ratioing systems as a replacement for optical-null because they hold some promise of avoiding the faults. A live zero can be obtained electrically with a simpler device than the light by-pass arrangement. Light chopping can be done on the source side of the sample so that there is no effect of sample radiation on the accuracy of transmission measurements. Also, it is surmised that the resistance function of a slide wire on which the ratio measurement is made would be more permanent than the control function of the light attenuator. Several systems are in use with good success in ultraviolet, visible and near infrared spectrometers. The design of a successful system in the high frequency regions of the spectrum is facilitated by the availability of fast response photo detectors for use at room temperature. With the more efficient sources and detectors available for use at short wavelengths, signal-to-noise ratio is not a major problem. In the medium infrared electrical beam-ratioing cannot be considered as a simple, easy means of avoiding the deficiencies of the optical-null system. To a

large extent it is trading optical and mechanical problems for electronic problems. This will become more apparent as we look at some of the systems which are in use or have been proposed.

A system was described in 1950.³⁶ Beam switching is done with an equal dark interval between each exposure. The signal is amplified and the portions derived from each of the two beams are separated by synchronous switches, rectified, filtered and recorded as the ratio of the two beams by balancing on a ratioing slide wire. This system is not immune to sample temperature effects on the transmission measurement. An analysis of the noise factor for the system gives the noise as 1.68 times the single beam or optical-null. This figure is the effective or rms value derived from a peak value of 2 at 100% transmission and $\sqrt{2}$ at zero transmission. Because of the exponential cooling curve of the thermal detector, some mixing of the signals from the two beams occurs, and the timing of the decoding switches is critical.

Another system, also published in 1950,²⁵ divides the aperture of the monochromator vertically between the two beams. Each aperture is chopped with equal on/off periods, 90 degrees out of phase with the other. The signals are detected by a single detector, amplified and separated by synchronous decoding switches, rectified and filtered, and the ratio measured on a slide wire. Since this system uses only half of the available aperture for each beam, the noise factor for either beam is twice that for optical-null. At zero transmission the reference beam does not contribute noise to the record so the noise is only that of the sample beam (i.e., 2). At 100% transmission there is addition of the two non-coherent noise signals for a total noise approximately $2\sqrt{2}$. Because the two beams are using different parts of the optics in the monochromator, extremely accurate optical surfaces and alignment are required or else one might have the two beams viewing wavelengths slightly separated. If this effect is present, a very undesirable pattern results when scanning through regions of atmospheric absorption. Instead of getting good cancellation of the bands, an up and down pattern is recorded as the two beams go through the absorption bands slightly out of phase. If the modulating disc is located between the sample and monochromator, this system will also respond to sample temperature.

These systems are discussed and their noise factor compared, along with several other systems, by Golay.²³

Applied Physics Corporation of Monrovia, California announced the Cary-White Model 90,¹¹ a double beam prism-grating spectrometer at the 1961 Pittsburgh Conference. This scans the range 2.5μ (4000 cm^{-1}) to 22.2μ (450 cm^{-1}) and uses an electrical beam-ratioing system. A few instruments of this model have now been delivered to users. The optical diagram is reproduced in Figure 3-16. Each of the two beams is chopped

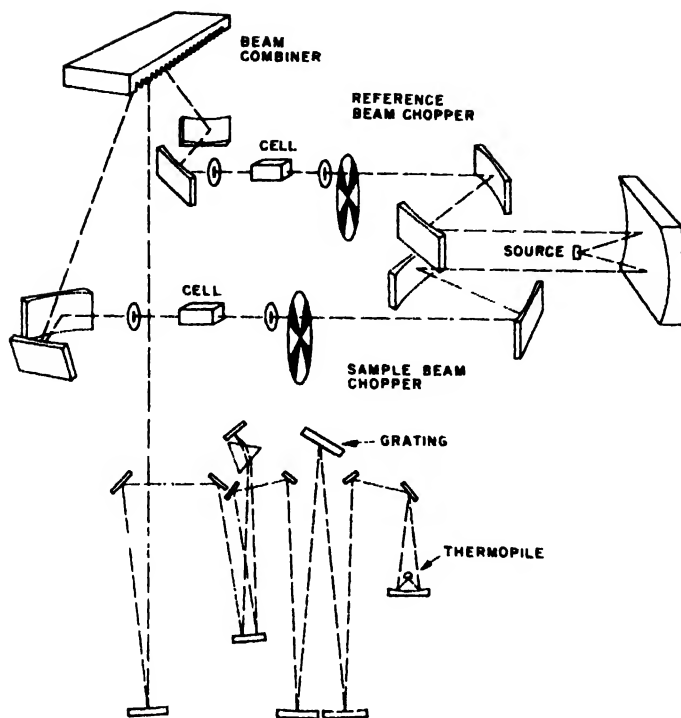


FIGURE 3-16. Commercial electrical ratio-recording spectrophotometer (Applied Physics Corp., Cary-White Model 90).

individually at C_1 and C_2 . The sample beam is chopped at $1\frac{1}{2}$ cps and the reference beam at $26\frac{2}{3}$ cps. The two beams are combined and mixed throughout the aperture of the monochromator by the step-like optical component. After passage through the monochromator, the light signals from the two beams fall on a single detector. After preamplification the signals are separated by tuned circuits on a frequency basis, further amplified, and the ratio is measured electrically. This system also shares the monochromator aperture between the two beams, to yield a noise factor of two, to which must be added any noise in ratioing the two signals (especially significant at 100% transmission). With the chopper location there is no transmission error due to sample radiation.

Instruments and Communications Corporation introduced at the 1964 Pittsburgh Conference a new filter-grating infrared spectrophotometer (designated the ICI 2000). This uses a system of electrical ratioing called phase nulling. In this system the two beams are chopped 90 degrees out of phase and the voltages added, to produce a composite signal with a phase angle

which varies according to the relation: phase angle $\theta = \arctan E_s/E_r$. Another pair of 90 degree out-of-phase signals is generated synthetically. These are also added, to yield a phase angle $\theta_s = E_{ss}/E_{rs}$. θ is compared with θ_s in a phase angle comparator system. If the phase angles are unequal, an attenuator adjusts E_{ss} until a null is produced. The recording pen is coupled to this attenuator, thus indicating the sample to reference beam ratio. At present no spectra showing performance of this instrument have been published so a complete evaluation cannot be made. Since chopping is done on the source side of the sample, it is apparent that the system successfully avoids errors in transmission measurements resulting from sample radiation. The noise factor is estimated to be equivalent to other electrical ratioing systems such as the Halford-Savitzky and Model 90 in which only half of the monochromator aperture is available to each beam.

Another system of electrical ratioing is used in some of the short wavelength range spectrophotometers, e.g., the Beckman Model DK-2A. The light from the source is chopped at a relatively high frequency, which can be considered as a carrier frequency. The interrupted light is switched alternately between sample and reference paths. With the PbS detector used in the DK-2A, the interruption and beam switching frequencies can be high (480 c/s for the interruption frequency and 15 for beam switching). In this high frequency range of the spectrum, the system gives excellent reproducibility of absorbance measurements and good signal-to-noise. The intensity of each individual beam is determined by the amplitude of the signal at the interruption frequency, which takes place on the source side of the sample, so there would be no problem of a contribution from sample radiation even at longer infrared wavelengths.

This system should be applicable through the medium infrared range with good chance of success, if one is willing to assume the trouble and expense of maintaining a photo detector at liquid helium temperature. Such a system has been described by Keahl at the 1962 Pittsburgh conference to cover 2.5μ (4000 cm^{-1}) to 9μ (1100 cm^{-1}), using alternately three photoconductive detectors cooled with liquid nitrogen.³⁸ Even with thermal detectors, the prospects of success are somewhat encouraging. If we begin with a minimum beam switching frequency of say 5 to 10 cps and use a carrier frequency of a minimum multiple of this (15 to 20 cps), the highest frequency required may not seriously reduce the detector signal amplitude. The entire aperture of the monochromator is used for each beam. So the noise factor appears favorable.

Another system of electrical beam-ratioing uses the same optical arrangement as optical-null systems except for elimination of the reference beam attenuator. The beam flickering mirror sector is modified with two dark sectors located between the beam crossover. A typical choice of the

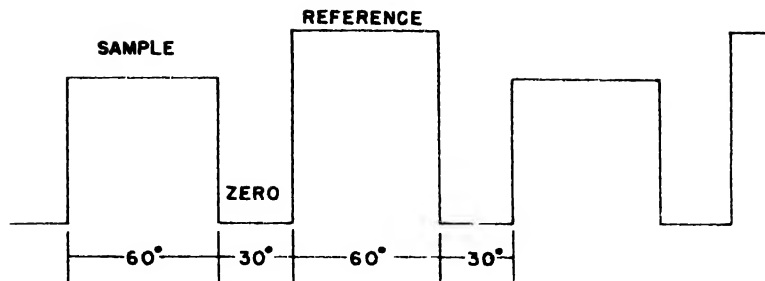


FIGURE 3-17. Beam-switching and chopping pattern for a method of electrical beam-ratio-recording.

chopping and beam switching periods is illustrated in Figure 3-17. This is the same modulation pattern as for the modified Hornig system²³ for which Golay calculates a noise factor of 1.11 compared to optical-null. A method of extracting the required information for deriving the ratio I/I_0 , which avoids the critical decoding switch and minimizes the filtering requirements, has been described.⁴⁵ The modulation system gives rise to a detector output signal which is a combination of two frequencies: an F frequency which is proportional to $I_0 - I$ and a $2F$ frequency proportional to the average of I_0 and I denoted by $\frac{I_0 + I}{2}$. The two frequencies are amplified, separated by selective electrical filters, and then rectified and filtered, providing DC voltages proportional to $I_0 - I$ and $I_0 + I$. When these are added and divided by 2 we obtain a value for I_0 . A self-balancing potentiometer is used to record the ratio $\frac{I_0 - I}{I_0} = 1 - \frac{I}{I_0}$. The desired ratio $\left(\frac{I}{I_0}\right)$ can be read directly simply by calibrating the scale in the required direction. This system was developed independently at The Dow Chemical Company Infrared Laboratory where a spectrometer using it has been in operation since 1959. Experience in operation of this instrument supports that the theoretical noise factor can be realized in practice. It is similar to optical-null in its response to sample radiation because the difference $(I_0 - I)$ signal is derived from beam switching after the sample location.

ELECTRONIC SYSTEMS AND OPERATING ADJUSTMENTS

Detector Amplifiers

Until the early 1940's almost all measurements of detector outputs were made with galvanometers. Amplification was accomplished by means of a small mirror attached to the suspended coil of the primary galvanometer.

Rotation of the mirror moved a spot of light across a pair of opposing photo-voltaic cells. This produced an unbalance in the photo cells, causing a much larger current to flow in a secondary galvanometer. The deflections of the secondary galvanometer could be recorded by again using an attached mirror and light beam lever. The moving spot of light was focused to a point through a long cylindrical lens onto a photo-sensitized paper. This paper was mounted on a drum driven through a coupling to the spectrometer scan drive. Developing the chart gave a photographic record of detector output vs wavelength. With the relatively heavy detectors in use at the time and with the long period galvanometers, the system was slow and was sometimes disturbed by building vibrations and thermal drifts. To eliminate the effects of drift, the need for interrupted radiation was recognized and Pfund devised a Resonance Radiometer in which the radiation was interrupted by a swinging pendulum in tune with the galvanometer period. Firestone introduced the use of electronic tube amplifiers in conjunction with photo cells and a galvanometer light-beam lever.¹⁶

Efforts to decrease the response time of these systems brought about the development of faster responding detectors.^{2,9,10,15,30,35,58,63,64} When practical interruption frequencies of at least 5 cps were attained, a switch to all electronic AC amplification was made⁵⁷ and is the system used entirely at present.

The principal pitfall in the design and use of an electronic amplifier with infrared detectors is to maintain the noise at a level where it does not add a significant contribution to the final output.

Noise is nearly always a limiting factor in the operation of an infrared spectrometer — that is, higher resolution would be used (narrower slits) and/or faster scan if the noise could be tolerated. An ultimate source of noise is the Johnson³⁷ noise of the detector. It can be calculated from the relation

$$V_j = 1.3 \times 10^{-10} (R\Delta f)^{1/2} \text{ rms volts at room temperature} \quad (3-13)$$

This turns out to be about 4×10^{-10} volts for a 10 ohm detector with Δf equal to 1 cps. The amplifier contribution should be less than half of this value, say 2×10^{-10} . The sources of noise in a vacuum tube are: (a) flicker noise arising from random emission of electrons from the cathode, (b) shot noise generated by random arrival of electrons at the plate, and (c) grid current noise. Flicker noise follows a reciprocal of frequency trend and is usually the predominant noise at the low frequencies used with thermal detectors. A good amplifier stage would have a noise equivalent of about 10,000 ohms in the grid circuit at six cps or about 1.3×10^{-8} volts. This is far from the required 2×10^{-10} volts but a transformer can be used, stepping up the ten ohm detector impedance to several megohms for the

input to the grid of the tube. This impedance ratio requires a turns ratio of around 300 to one, and a practical voltage gain of about 200 can be realized from the transformer. If the noise voltage of 1.3×10^{-8} from the tube is referred to the primary of the input transformer, a noise well below the desired 2×10^{-10} volts is obtained. Great care is required in the selection of the input transformer in order to assure that it does not contribute appreciable noise itself. This requires one with relatively low resistance of the windings, high reactance to accommodate the low frequency of operation, and extremely good shielding to minimize voltages induced by stray magnetic fields.

In assembling and wiring the first stage of amplification, only wire wound resistors should be used to avoid the current noise usually associated with carbon resistors. An important consideration also is the way in which the tube acquires grid bias. It has been shown that a reliable method is the introduction of a high DC impedance in the grid circuit.⁵⁰ This may be done by coupling the grid to the input transformer secondary through a good quality paper film capacitor of about 0.2 to $0.5\mu\text{f}$ capacity. This may be left as the only direct current grid return path, or, if the application requires prevention of grid blocking, the capacitor may be shunted with a special low-noise type 100 megohm resistor. Often much can be gained in regard to noise reduction by tube selection for the first amplifier stage. Generally, good and bad tubes are found among different types and different manufacturers, but certain types made by certain manufacturers sometimes provide a better than average yield in the percent of usable tubes from a number tried.

These extreme precautions in regard to noise need be considered only for the first stage. For the second stage ordinary precautions should yield good results because the effects of noise from the latter are reduced by the reciprocal of the gain of the first stage (100 or so).

To determine the total gain of the low frequency amplifier including the input transformer, it may be assumed that it is desired to have the calculated Johnson noise of 4×10^{-10} volts appear at full gain as 1% on a 50 millivolt recorder. The loss in the filter after the signal rectifier must be considered and will be assumed to be 100. The required output voltage from the amplifier with these assumptions, calculates to be .05 volt from the 4×10^{-10} volts noise input, requiring a gain of 1.2×10^8 . This represents the maximum available gain and would rarely be used.

One other function which can be handled very conveniently by the amplifier is bandpass limiting. This may be done with a twin T feedback network.²¹ The network has high impedance at the design frequency with minimum feedback and maximum gain at this frequency. At all other frequencies feedback is present, reducing the gain. If the band pass is too

narrow, control can be effected by shunting the parallel T network with a resistor in the vicinity of 20 megohms. For the sake of gain stability, it is desirable also to include other non-selective feedback loops.

The power supply for the amplifier should use voltage regulation of the plate supply and itself be fed from a line voltage regulator. At least the first stage and possibly the second stage heaters should be supplied with filtered direct current to minimize line frequency voltage mixing in the signal circuits.

The exact design of the detector amplifier should take into consideration the application for which it is to be used. For example, a very high degree of linearity and gain stability is required for electrical ratioing systems but the requirements for optical-null are only moderate. A detailed circuit of a practical detector amplifier is shown.⁵⁸

For convenience in the operation of an output signal full-wave rectifier, it is desirable for the amplifier output stage to provide both phases, 180 degrees apart. This may be a center-tapped output transformer or a resistance-capacitor circuit. Regardless of the application, a synchronous rectifier phased from the radiation modulator is either required for direction sensing as for optical-null, or preferred for the inherent advantages of linearity and discrimination against other frequencies and out-of-phase voltages from the detector signal.

Special Electronic Accessories

Automatic Speed Suppression. The scanning rate of an infrared spectrometer is limited by the response time of the recording system - that is to say, by the ability of the recording system to follow the changes in sample transmission because of certain time lags in the system. The time lags include the amplifier bandpass, filtering of the demodulated signal, and the balancing speed of the servo system (determined by damping, gear ratios, and inertia). These lags are introduced for the most part intentionally to reduce the noise appearing on the recorded spectrum. They can be combined and described as the bandpass of the total system, and recorded noise would be proportional to the square root of the bandpass. From these considerations it is apparent that the quality of spectra can be improved to the extent that the scanning time is increased. Automatic scan speed suppression has been devised as a scan-time saving means, while still retaining the noise attenuating benefits of a relatively long recording time constant. This is possible by recording at relatively high speed through regions of no absorption bands and recording at a slower speed through the absorption bands. This scan speed control is accomplished by using the unbalance signal to control the speed of the scan motor. A typical system might be adjusted to reduce scanning speed to $\frac{1}{2}$ by a 1% off-balance

signal. A convenient means of determining the optimum settings of normal scan speed and the degree of speed suppression, is to select a portion of a spectrum which should include a range of weak to strong, and narrow to wide bands and then scan it first at a very slow speed. Then scan this same portion at increasing rate up to the highest rate at which a satisfactory duplication of the slow-scan record can be obtained with the best adjustment of the degree of speed suppression.

Automatic Gain or Slit Control. The slit-program cam on a per cent transmission recording spectrometer is made to provide constant reference beam intensity as nearly as possible throughout the range of the spectrometer. The slit control is adequate when there is no reference sample used and the spectrometer light path is purged with dry CO₂-free air. At times it is desired to obtain difference spectra with the use of a compensating sample in the reference beam. If this is done, there are likely to be regions of low transmission in the reference beam, causing a loss of loop gain in the servo system with sluggish pen response. To compensate for the loss of reference beam intensity, it is desirable to increase amplifier gain or increase slit width. This is fairly easy to accomplish in an electrical ratioing spectrophotometer because a signal proportional to the reference beam is normally present and it can be monitored and used to control amplifier gain or slit width. In an optical-null spectrophotometer there generally is no such signal available. A system for producing the signal in an optical-null system was developed and described.¹⁴ It uses a narrow dark sector on each side of the beam switching mirror. This system of chopping gives rise to a $2f$ signal with an amplitude proportional to the sum of the sample and reference beam intensities. But the reference beam is attenuated to match the sample transmission, so, to make the $2f$ signal usable as an indicator of the unattenuated reference beam intensity, a correcting factor proportional to pen balance position must be introduced. A system to accomplish this is described. Some commercial versions now available use a non-linear potentiometer coupled to the pen-drive to modify the $2f$ signal so that it is independent of pen position down to 5 or 10% transmission of the sample. The automatic gain or slit control can effectively maintain the response of the recording system even where only a few per cent is transmitted by the reference sample. In regions of complete reference beam absorption, however, there is a hopeless condition and no useful information can be obtained from a compensated scan through them even with the use of automatic gain or slit control.

Operating Adjustments

The operating adjustments of an infrared spectrometer are very important. One may possess the best instrument available but unless it is

used with careful and systematic adjustments of the controls, and unless performance is observed critically for the earliest evidence of malfunction, the results may be far less than the capabilities of the instrument.

The modern infrared spectrophotometer has a number of controls which offer a choice of a wide range of operating conditions. Often the adjustments are interrelated so that an adjustment may require the resetting of one or more other variables. In general, there are three primary variables: scan time, signal-to-noise, and resolution. There is some freedom of choice for any two of these, while the third would then be largely determined by the choice of the other two. For example, one might choose a scan time and signal-to-noise level. The choice of scan time will determine the response time setting which will permit the balance system to record the absorption band contours with sufficient accuracy. Now that the response time or bandpass has been chosen, the absolute noise voltage ideally is determined by the detector noise. To get the chosen signal-to-noise ratio, only the signal can be controlled, requiring a slit program adjustment. There is no choice of resolution, since it has been determined by the slit program required to provide the chosen signal-to-noise.

Of the remaining variables, servo loop gain is probably most critical in its effect on spectrometer performance. Spectrometers often have separate servos for pen positioning and for reference attenuator positioning. The former is merely a transmitting slide wire and follow-up system and the latter is a feed-back loop which includes the reference beam attenuator, the monochromator optical path, the infrared detector, the low frequency amplifier, demodulator, filter, line frequency inverter, servo amplifier, and the attenuator drive system. If both of these servos are used, approximately the same procedure for setting each can be used. It is well to begin with the pen servo and adjust for zero to one tenth per cent dead spot while avoiding the symptoms of instability ("hunting"), indicating excess gain. The gain adjustment for the reference beam attenuator is much the same except that one overshoot of about 3 to 5% of full scale can be expected in response to a step change of about 25% or more in the sample beam transmission. After these adjustments have been established initially, it is very desirable to measure and note the signal outputs, such as the off-balance output voltage, for a certain per cent off-balance. This affords a convenient means of repeating the original settings and improves the consistency of the day-to-day performance of the spectrophotometer.

ACCESSORIES FOR SPECIAL SAMPLES

The manufacturers of infrared spectrometers generally have developed for use with their instruments a rather complete line of accessories to facilitate obtaining spectra, using the many special techniques available.

Beam Condensers

These devices are extremely useful in obtaining spectra of minute quantities of materials. By their use, qualitative spectra for identification of material of less than a microgram can be secured. A short piece of fiber or a flake of "dirt" from scrapings of a coating are typical examples of samples. These may be ground and pressed with powdered KBr into a pellet, dissolved in a minute amount of solvent, and deposited in a small cavity cell or run intact as a small area film.

The simplest type of beam condenser uses convex lenses in a straight-through arrangement. The first lens provides about a $\frac{1}{3}$ size, reduced image of the slit at the sample position. The second lens restores the original image size and beam convergence required for the entrance slit.

A second type of beam condenser uses all reflecting optics, thus avoids chromatic aberration and can give a somewhat higher ratio of image reduction. An optical diagram of this type is shown in Figure 3-18. This particular accessory gives a six-to-one reduced image of the slit at the sample position, approximately equal in size to the 2 mm by 0.2 mm detector of the spectrometer.

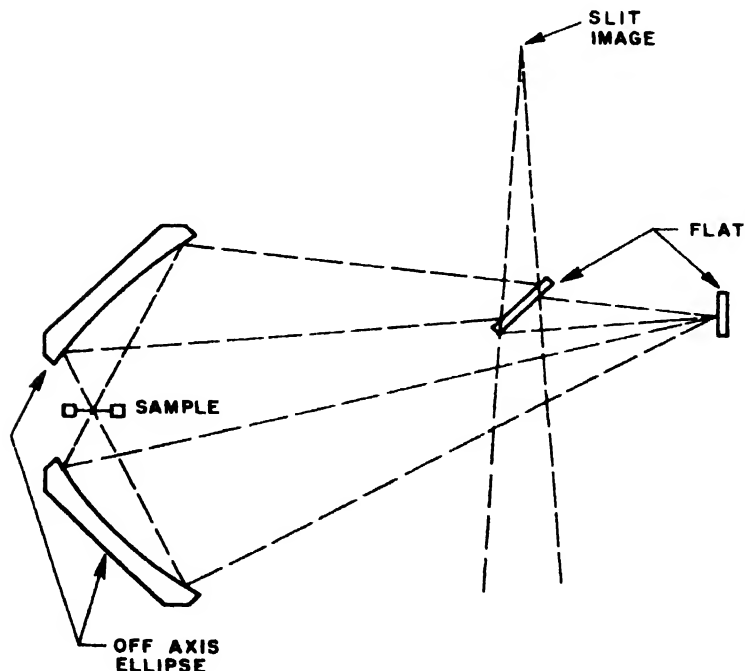


FIGURE 3-18. Sample beam condensing system using reflecting optics.

The spectrum of even smaller area samples can be obtained by masking any uncovered area, but, of course, a corresponding loss in signal will result.

Long Optical Path Gas Cells

The purpose of this class of accessory is to obtain spectra of gases when their concentration is too low to get the required absorbances in the simple straight-through gas cell (such as ten cm). This generally requires that the diluent gases be principally nonabsorbers. A typical example is for the detection and identification of toxic vapors in the atmosphere or room air. The path-length-to-volume ratio for these cells is excellent but the absorbance is related to the pressure to which the cell is filled and if sufficient volume of gas is available, can be used at several atmospheres of pressure. Concentrations of less than one part per million of most gases can be determined.

The optical arrangement generally used is the multiple reflection one, according to White.⁶⁶ A typical cell available commercially has a maximum of forty meters path length in forty traversals which can be reduced to any smaller number divisible by four, as 36, 32, 28, etc. The volume is about 50 liters.

Attenuated Total Reflection

Usually called ATR, this technique was proposed by Fahrenfort in 1961¹⁴ as a method to obtain the spectra of certain forms of samples which for one reason or another do not yield to the more usual methods. Some examples could be very viscous or solid materials which are insoluble in the usual solvents, opaque materials, or coatings on opaque material. A

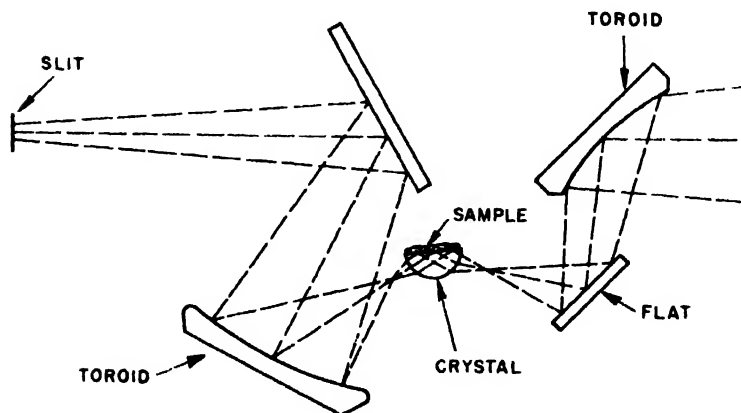


FIGURE 3-19. Optical diagram of attenuated total reflection sample measuring accessory.

promising possible application is for a process stream analyzer for a viscous or nearly opaque material. With this method the requirement for flowing the material through a thin cell could be avoided. An optical schematic of one of these accessories is shown in Figure 3-19.

Polarizer

The principal application of this accessory is to determine the presence of orientation of the molecules in a sample material such as might be the case with a polymer film stretched along a certain axis in the manufacturing process. If two spectra are recorded of such a sample, each one at a position of orientation rotated 90 degrees with respect to the polarized radiation, it is possible by comparing the two spectra, to determine the direction and the functional groups that are polarized.

A reasonably efficient polarizer for the medium infrared range can be made by an array of a series of five or six polarizing transmission plates in the path of the radiation. The plates are spaced a small distance apart and oriented at an angle to the beam so that the angle of incidence equals $\arctan n$. This is known as the Brewster angle. In this position, light whose electric vector is polarized in a direction perpendicular to the axis of inclination, will be weakened by reflection loss at each plate. Finally, the emerging beam has a relatively high degree of polarization with its electric vector perpendicular to the axis of inclination of the plates.

Silver chloride is a nearly ideal material to use for the polarizing plates for the medium infrared range. It has a high index of refraction yielding the relatively high Brewster angle of 63.5 degrees. It can be used in very thin plates and this minimizes the lateral shift due to refraction of the transmitted component.

INSTRUMENTATION FOR THE FAR INFRARED

Far infrared instrumentation is being considered separately because of some special problems associated with work in this region of the spectrum.

Window Materials

Scarcity of window materials is a handicap. No suitable prism materials are known. CsI, the longest wavelength transmitting alkali halide, can be used in thin windows to about 50μ . Crystal quartz, opaque from about 4.5 to 45μ , is a very useful material for filtering out the medium infrared and can be used for cell windows in thin plates to continue to longer wavelengths from the transmission limit of CsI. Polyethylene film is widely used for windows of gas cells but because of the lack of rigidity, is not very practical for thin layer liquid cells. If the right type of film is obtained

it is essentially free of bands throughout the region beyond 25μ . Some types evidently contain an impurity, exhibiting absorption $\approx 200\text{ cm}^{-1}$. Diamond is the only known inorganic material transparent throughout the medium and far infrared and it is very useful for detector windows. Only pieces of up to about $\frac{1}{4}$ -in. diameter are available at a practical cost. Such windows could be used in a far infrared microcell to be used with a reflecting beam condenser such as described in a preceding section. None of these materials is suitable for a dispersing prism. Gratings are used exclusively for the dispersing elements in the far infrared.

Sources

The usual types of thermal sources can be used but the radiant power is very low, falling off according to Planck's radiation law as shown in Figure 3-1. Some improvement is procured with a high pressure quartz tube mercury arc source. From about 70μ this source exhibits radiation in excess of that from a thermal black body radiator at a corresponding temperature. The mechanism of this radiation is not thoroughly understood. The quartz envelope is heated to incandescence from the operation of the arc and serves as a suitable thermal radiator throughout the region where it is opaque. In the region of wavelengths shorter than 4.5μ where quartz is transparent, there is no significant radiation. This is an extra bonus in using this source for the far infrared because the requirements of separating that part of the spectrum from the desired part is not encountered.

Detectors

Certain features of the Golay pneumatic detector make it very useful for this part of the spectrum. The relatively large area of the receiving surface is required because of the wide slits used at long wavelengths. At some wavelengths the slits may be opened to become square (as wide as their height). In addition, the uniform absorptivity of the receiver throughout the range is very beneficial. Some progress is being made in development of thermocouple detectors for this region and good results have been reported using helium-cooled carbon bolometers.²⁰

Monochromator Systems

In the past, monochromators for the far infrared have been characterized by a series of measures whose only purpose is to remove higher orders diffracted from the grating dispersing element. These measures include:

(a) crystal chopping — effective because the detector does not respond to the part of the spectrum where the chopping crystal is transparent, since it is unmodulated.

(b) residual ray reflection (restrahlen) plates -- these have strong (up to 98%) reflection bands in the far IR. By selection of the proper plate for specific regions, a wide range may be covered.

(c) gratings used as scatter reflection plates - wavelengths greater than about twice the grating spacing will be reflected in the zero order while shorter wavelengths will be diffracted by the grating.

(d) transmission filters such as carbon black impregnated polyethylene and crystal quartz.

Several spectrometers of this type have been described.^{7,46,48,52,72} Generally the optical-null photometer system has been avoided because this would not permit the use of crystal chopping.

An instrument using the interferometer principle has been developed and is available commercially.¹⁸ The interferometer supplies an interferogram with the data on punched paper tape. A standard transmission spectrum can be derived from this by submitting the punched tape data to the operations of a large size digital computer.

It appears that the far infrared portion of the spectrum will become no more difficult to use than other infrared regions with the introduction of a new spectrometer by Beckman Instruments, Inc. at the 1964 Pittsburgh Conference. Keahl, Sloane, and Lu³⁹ have extended the development of a set of long wavelength cut-on filters which allow the filter-grating principle to be used in the far infrared similar to systems being used in the medium infrared. The instrument designated Model IR-11 using these filters provides a scan in about 15 min from 12.5 to 300 μ . The method of producing the filters has not been disclosed but further development of the type described⁷¹ would show promise of meeting the requirements.

In working in this region of the spectrum, special consideration must be given to the removal of atmospheric water vapor in the spectrometer path. This is true even in the case of a double beam type instrument because of the intensity of these absorptions. It is not sufficient to merely balance them out. This would result in a serious loss of energy. Best results are obtained if the spectrometer case can be evacuated and the sample space purged. If the spectrometer case is not evacuated, a rather high volume purge of extremely dry air would give satisfactory water spectrum removal with the double-beam principle.

For an extensive bibliography of publications relating to far infrared, Ref. 49 is recommended.

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CHAPTER

4

Sample Preparation Procedures

David N. Kendall

IMPORTANCE OF SAMPLE PREPARATION

Solving a problem by infrared spectroscopy involves three basic phases — sample preparation, instrumental scanning of spectra, and interpretation of the spectra. Each phase is of equal importance. Neglect of any one leads to errors or inadequacies in the final results. Even at optimum performance, e.g., no spectrophotometer can yield a satisfactory spectrum from a poorly or improperly prepared sample. Time spent selecting the best sampling procedure and preparing the sample carefully and adequately is essential.

Fortunately, infrared techniques are amenable to almost all materials regardless of physical state, color, morphology, molecular weight, number of components, solubility, or number of phases present. While metals are normally not studied or analyzed through infrared methods, certain ones such as germanium, e.g., yield useful absorption spectra.

Novel and useful sampling techniques are continuously being discovered. As experience increases, the spectroscopist may through necessity devise sample preparation methods himself. The particular methods most appropriate and most useful for any given laboratory will be governed to some extent by the type of problems confronting the laboratory.

SOLIDS

There exist more techniques for preparing a solid specimen for the infrared spectrophotometer than for any other physical state of matter.

As noted in Chapter 2, Pfund first clearly pointed out that the particle size of solids should ideally be less than the wavelengths of the incident radiation to obtain the most satisfactory absorption spectrum, all factors considered. When this condition obtains, refraction and reflection do not occur because a wave front of coherent radiation cannot be formed. Rayleigh scattering can still take place at every phase boundary. Such scattering is far less a problem, however, than that by refraction and reflection of large particles. Moreover, the magnitude of Rayleigh scattering is a function of the square of the refractive index of the two phases. By suspending the particles to be scanned in a medium whose refractive index is as close as possible to that of the particles, this type of scattering can be minimized.

The majority of infrared spectral studies begin at 2μ at the beginning of the fundamental infrared region. It is desirable, then, that all solid particles in a sample for scanning be reduced in size below 2μ . Since *all* of the particles usually can't be reduced to below the 2μ level for a solid sample prepared by either the mull or pressed halide disk technique, often the transmission of a sample rises sharply from 2 to about 4μ . This results from the "scattering" of radiation by those particles larger than the irradiating wavelength. The steepness of the slope gives a measure of the scattering. Very vigorous grinding of a sample is required to eliminate this scattering entirely and obtain a flat background between 2 and 4μ . Since quantitative work is best done in solution whenever possible, eliminating this slope entirely on qualitative scans is mostly an esthetic exercise.

Another benefit obtained by reduction of as many as possible of the particles to a size below 2μ is minimization of the Christiansen effect. This effect arises when the refractive indices of a solid particle and its surrounding medium differ appreciably. The refractive index of any material has a discontinuity at each strong absorption band. The refractive index falls sharply on the high frequency side of an absorption maximum from its value in regions of no absorption and approaches the true absorption peak asymptotically. The refractive index also falls sharply on the low frequency side of an absorption maximum but from an initial high value asymptotic to the true absorption peak. Because this refractive index discontinuity occurs at the true absorption peak, the observed absorption is a distorted one with its frequency slightly less (wavelength slightly greater) than the true absorption peak. This distortion arises from the varying relation between refractive index of the particles and that of the surroundings. The two are more nearly equal on the high frequency side of the absorption maximum but differ widely on the low frequency side. The Christiansen effect is normally most pronounced at short wavelengths because a larger number of solid particles will have size comparable to the wavelengths irradiating them. While the effect cannot be completely eliminated, it is minimized by pre-

paring as many particles as possible to be below 2μ in size and by dispersing the particles in a medium having a refractive index close to that of the particles.

An additional reason for reducing the particle size of a solid as much as possible before scanning is to assure uniform coverage to the infrared beam area. If such coverage is not obtained, there will be small areas over which no particles at all are met by the irradiating beam. The true inherent absorbance of absorption bands will therefore not be obtained. To obtain accurate absorbance values the infrared beam area must be uniformly covered by small sized (below 2μ) particles.

Whenever solid samples are prepared for infrared scanning, consideration must be given to the possibility of polymorphism. Both organic and inorganic materials are prone to exist in two or more different crystalline forms — polymorphs. Since the infrared spectra of polymorphic forms of the same substance are different, it is necessary that meaningful spectral comparisons be made on the same polymorphic forms. Grinding, temperature change, influence of the matrix in a mixture, e.g., can cause transformation from one crystalline form to another. Because the transformation is not necessarily complete, polymorphic mixtures can occur. When the spectra of two solid materials are different and other physical evidence and sample history suggest the two should be identical, the possibility of polymorphism should be considered. If two samples yield different spectra in the solid state but identical spectra in solution, polymorphism is the reason. Unfortunately, when seldom encountered, it is easy to forget polymorphism can be the origin of "spectral differences" in "different" materials.

Oil Mulls

The principal preparation procedure for solids is the time honored oil mull technique, generally called the "Nujol" mull after the trademark for a popular brand of highly purified mineral oil. Nujol is a mixture of very largely straight chain saturated hydrocarbons averaging about C_{25} . It contains practically no aromatics or olefins or other impurities, has a helpful viscosity, and a refractive index which minimizes the difficulties of obtaining accurate spectra in the solid state.

An oil mull is made by grinding and dispersing a solid material to as fine a particle size as possible in Nujol or other mineral oil. The resulting paste is then spread out between flat NaCl or KBr plates by hand pressure to the desired thickness, mounted in a metal cell, placed in the sampling grooves of the spectrophotometer, and scanned over the desired wavelength range.

There is more art and science in the preparation of a satisfactory mull than one might realize from watching the preparation. While some samples

require an agate mortar and pestle, a few even a boron carbide mortar, the general run of organic materials and some inorganics the spectroscopist scans can be conveniently milled on plate glass using a paint muller, commonly used in the paint industry for tinting-strength determinations. This is true because very many materials one desires to scan are already in a finely divided state and simply require uniform dispersion in the oil.

Normally, about 5 to 10 mg of solid sample is placed on the plate glass, a drop of Nujol from an eye dropper put in the center of the glass muller, and "elbow-grease" applied to vigorously grind and disperse the solid particles in the Nujol. "Grinding" in this context means breaking up larger aggregates into the fine ultimate particle size already existent in the crystalline, granulated, or powdered sample. After about 15 circular strokes with the muller, the sample-oil mix is scraped from both the plate glass and the muller with a stainless steel spatula, placed in one small spot on the plate glass, and the "grinding" process repeated. Usually, three such operations will be sufficient to complete the mull, occasionally two, sometimes four or more. Depending on the consistency obtained, more Nujol or more sample may need to be added during the mulling operation. Experience with mulling a variety of solid samples will soon give one a feel for the proper proportions of Nujol to solid for any given type of sample.

An adequately prepared mull will usually be translucent to visible light. When viewing the mull squeezed out between the salt plates to the desired thickness, no cracks, graininess, or other irregularities in the uniformity of the film should be evident. If such irregularities are present, the mull will yield scattering of the radiation at short wavelengths, distorted absorption peaks and transmission maxima will be obtained, and the spectrum recorded will be of little value, or worse, will be entirely misleading. The adequacy of the mull can be judged by noting the slope of the spectrum between 2 and 4μ . Ideally, a straight background line (I_0) should be obtained in this region. The worse the deviation from linearity, the greater the scattering and the poorer the mull and the recorded spectrum. Some slight upward slope in I_0 from 2 to 4μ can be tolerated, and experience and comparison of one's spectra with reliable literature spectra enable one to judge how much scattering can be tolerated without loss of accuracy and precision.

Most metal cells commonly used to hold the salt plates containing the mull film have elliptical or circular holes in both the fore-plate and back-plate to allow passage of the infrared beam. The back-plate commonly contains either two or three threaded rods just beyond either end of the holes in a one-and-one or two-and-one arrangement. These rods fit through appropriate holes in the fore-plate and the two metal plates together hold the salt plate mull sandwich by means of knurled nuts adjusted to the

desired pressure. It will be found useful to maintain uniform finger pressure on the whole mull sandwich while the nuts are screwed down. Otherwise, the uniformity of the mull is apt to be destroyed, resulting in cracks or other irregularities. In the writer's experience, a metal back-plate with the two-and-one rod arrangement gives readier control over the uniformity of a mull than the one-and-one arrangement.

The thickness of the mull film required to yield a satisfactory spectrum will depend on the absorptivity of the sample. If the thinnest film that can be attained with a mull yields too strong a spectrum, dilution with Nujol (remulling) can be resorted to. Conversely, if the thickest film that can be attained yields too weak a spectrum, more sample can be added and the whole remulled. In this latter case, it often saves time to lay a piece of 0.005 in. "Nichrome" wire between the salt plates, at their extremity and out of the beam area, to realize a thick enough film. This immediately-made-wedge-shaped cell can eliminate the necessity of remulling.

What is a satisfactorily intense spectrum? For general qualitative purposes, a spectrum whose strongest absorption transmits about 5% of the radiation is desirable. There will, of course, be occasions when more or less intense spectra are desired. The spectroscopist, e.g., may want to scan an increased thickness mull over a region of very weak absorption or no absorption to determine whether a very weak band is real or simply "noise," or to make more sensitive the qualitative detection of a component suspected to be present at low concentration.

Tabletop spectrophotometers which allow a "dry run" of a mull quickly running through the spectral range by hand movement of the drum, e.g., with the pen not engaged to the preprinted chart paper - are time savers in the preparation of desired thickness mulls. Adjustment of mull thickness can be made before the recorded spectral run begins, rather than after the first complete scan has been finished.

Some samples will require an agate mortar and pestle for adequate mull preparation. A large, smooth-surfaced mortar facilitates the mulling operation. Use of a rubber policeman, rather than a spatula, to remove the mull from the mortar will prevent scratches and other surface irregularities developing.

Some samples will mull only with great difficulty; others not at all. Certain starches, e.g., will not yield even to the most vigorous grinding. When excessively long grinding of a sample eventually produces a satisfactory mull, additional mulls of like samples can be speeded by first grinding the sample in a mechanical vibrating mill, using a stainless steel vial and stainless steel balls. The final dispersion in Nujol is then easily made on the plate glass with the glass muller. The "Wig-L-Bug" and the solenoid type of vibrating mills are examples of such mills available from infrared suppliers.

For samples that will not mull, sometimes special treatments will make them mullable. Chilling a solid from room temperature to acetone-dry ice or liquid nitrogen temperature occasionally works. Heating a thick film material to just below its flowing temperature followed by immediate rapid cooling may induce mullability. Extensive grinding in the roller type ball mill may produce results.

For intractable plastic or rubbery materials, filings can often be made from which a satisfactory mull can be prepared. For those solids which still resist any of the above techniques, the pyrolysis procedure, discussed later on, can be used.

Excellent spectra for qualitative purposes can be recorded from properly prepared mulls. The mull technique is the simplest and most generally satisfactory method for obtaining a qualitative spectrum of a solid sample, when applicable. This technique does have some difficulties and drawbacks.

Nujol itself shows the absorptions typical of a long chain alkane hydrocarbon—very strong absorption from 3000 to 2800 cm^{-1} (3.5μ region), a strong band about 1460 cm^{-1} (6.85μ), a moderate intensity band about 1375 cm^{-1} (7.27μ), and a weak band near 722 cm^{-1} (13.85μ). These bands arise from hydrogenic stretching and deformation modes of the C—H groupings present. When Nujol mull spectra having high ratios of Nujol/solid are concerned, certain other normally very weak Nujol absorptions must be reckoned with—such as those about 1300 and 970 cm^{-1} .

One drawback of a Nujol mull spectrum, then, is that little if anything can be learned about the sample's absorptions in those regions where Nujol itself absorbs. With a little extra effort, this difficulty can be ameliorated. A second mull sample can be prepared and scanned, using a nonhydrogenic mulling agent. Perhalocarbon oils, such as "Fluorolube" or perfluorokerosene, can be used, or hexachlorobutadiene (HCBD), (hexachloro-1,3-butadiene). None of these liquids absorbs where Nujol does. By using a HCBD mull, e.g., together with the Nujol mull, one is able to obtain the complete 2 to 15μ range spectrum of a sample devoid of mulling agent absorptions. For the second mull, e.g., the spectroscopist scans only from 2 to 4 , 6.5 to 7.8 , and 13.5 to 14.3μ . In the author's experience, HCBD has been found quite satisfactory as the companion mulling agent to Nujol.

Another drawback to mull spectra is their lack of quantitative applicability. Adequate control over sample thickness, dispersion uniformity, and paste density cannot be maintained. Even use of internal standards and ratio methods (see Chapter 2) will not result in satisfactory quantitative analyses from mulls. Semiquantitative requirements can, however, be met.

For plastic- or rubber-like materials, which are very difficult to grind and for which a solvent can be found, it may be simpler to prepare films cast from solution as a sample preparation technique rather than use the mull procedure.

Extremely hygroscopic materials often yield poor mull spectra because the moisture absorbed by the sample is incompatible with the mulling agent yielding a poor dispersion, in addition to the strong obscuring water absorptions. Such samples can be mull in a dry box, or the technique described by Potts⁹ used. Near the conclusion of the mulling process 2, 2-dimethoxypropane is added to the mull paste. At pH below 7 this liquid reacts with water present yielding the volatile methanol and acetone, which latter two will evaporate as the grinding proceeds. Once the nose and the abrupt viscosity-increase in the mull paste tell that the volatiles have vanished, the mull is immediately placed between salt plates and scanned.

A final drawback of the mull technique is the possibility of a change in polymorphic form brought about by the grinding operation. Luckily, few solids are so sensitive to the mild conditions of the usual mull dispersion procedure.

Melts

When a solid sample has a low melting point, melting without decomposition, sublimation, or other chemical change, a few milligrams of it may be melted between salt plates in an oven, the resulting liquid squeezed between the plates to the desired thickness film, and allowed to resolidify as it cools. The infrared spectrum of the solidified melt is then scanned in the usual manner. Naphthalene is an example of a solid which yields an excellent melt spectrum.

The melt procedure is useful for low melting waxes and similar materials. It is helpful to place the metal cell backing plates into the oven along with the solid melting between salt plates. When the sample is molten, the whole cell can be put together and the metal plates screwed down to give a film of the desired thickness without cracking the salt plates. This can happen when warm salt plates touch cool metal backing plates.

When applicable, the melt method is quite satisfactory for qualitative purposes. Caution should be exercised in spectral comparisons melt spectrum vs melt spectrum, not melt spectrum vs mull spectrum, e.g. because orientation effects and polymorphic changes can occur.

The melt procedure also has limited quantitative value. When quantitative solution methods can't be developed for a solid sample, or where time requirements coupled with limited accuracy requirements dictate a simple, fast technique, a quantitative melt technique may suffice. Use of a wedge-shaped cell facilitates such an analysis, since it enables one to duplicate sample thickness with reasonable accuracy by moving the cell about in the infrared beam until a desired transmission maximum is reached from sample to sample. For routine quality control of production to given specifications, the melt method, where applicable, is a tidy one. The author has

worked out several such methods successfully, involving, e.g., rubber chemicals and naphthalene derivatives.

Films from Solution

Polymeric and other film-forming solids which are soluble in reasonably volatile solvents can be prepared for spectral scanning by casting films from solution and evaporating off the solvent. The films can be cast directly onto NaCl or KBr plates for solvent-soluble materials or onto AgCl disks or plates for water-soluble polymers. The solvent is evaporated by heating in an ordinary or vacuum oven. The film and halide plate are then placed directly in a cell for spectral scanning of the type previously described to hold oil mulls.

Heat and stirring usually speed up the dissolution process for polymers, and for some such as polyethylene, e.g., boiling benzene dissolves but room temperature benzene does not. For low boiling solvents, such as acetone, methyl ethyl ketone, and the like, it is not necessary to warm the salt plates before casting the boiling solution. For high boiling solvents, such as *o*-dichlorobenzene, it is wise to warm the salt plates to about 95°C before casting films. It is time saving to cast about three films of varying thickness on separate plates—one very thin, one medium thick, and one thicker than the other two. Then a film of thickness to yield an optimum intensity spectrum is usually assured. If no one of the three films proves to be the desired thickness, then two or all three of them may be placed atop each other to obtain the desired thickness. Here again it is helpful to have available a spectrophotometer on which a quick "dry run" can be made to facilitate selection of optimum film thickness.

The film-from-solution technique readily gives a spectrum satisfactory for qualitative identifications and other purposes free from interfering absorptions. It is ordinarily not desirable to try to develop quantitative methods on cast films because of the inability to measure film thickness with sufficient accuracy. Ratio methods can be employed, however, to determine components in copolymer or terpolymer systems, as indicated in Chapter 2.

Solvents used to prepare cast films must meet certain criteria: they must be able to dissolve the material, be reasonably low boiling, unreactive with the sample, and readily evaporated from the film. For a number of polymeric materials it is virtually impossible, without excessive expenditure of time, to vaporize off all traces of the solvent. It is therefore wise, immediately after scanning the spectrum of a film prepared by this technique, to first check the film spectrum for residual solvent absorptions. If one or two such are present, this can be taken into account in subsequent interpretation and identification. If no sign of the strongest absorption band of the solvent

is present, then good evidence has been found that no solvent absorptions can be present.

Linear polymers usually dissolve in benzene or toluene. Vinyl types can be handled with methyl ethyl ketone (MEK), cyclohexanone, or dimethyl sulfoxide (DMSO). Acetone dissolves a number of polyesters, phenolics, and other polymers of high oxygen content. Acetone or MEK are a good starting point for an unknown polymer, since they are easily vaporized if the attempt at dissolution proves unsuccessful. Ethyl acetate is most useful for cellulose derivatives. MEK will dissolve many epoxy resins. Elastomers and polyethylene can be dissolved with *o*-dichlorobenzene (ODCB). Polyethylene is readily soluble in boiling benzene or toluene. Many silicones are soluble in benzene. Some amino-formaldehyde and phenol-formaldehyde polymers are partially soluble in alcohols. Polystyrene and a number of coumarone-indene resins are soluble in benzene. Solvents for "Teflon" are virtually unknown, but "Kel-F" can be handled with fluorobenzene. *N,N*-dimethyl formamide (DMF) will dissolve nylon and other polyamides, heterocyclic nitrogen ring polymers, and a number of others. While it is among those solvents difficult to remove completely from polymer films, DMF has solubility for a wide range of polymer types.

If the investigator finds an unknown polymer will not dissolve in MEK, benzene, DMF, DMSO, or ODCB, he is then quite sure that the film-from-solution technique is not applicable to his solid unknown. Filings may be taken for an oil mull. Perhaps a thin film can be pressed out with or without heating. Or pyrolysis will have to be resorted to.

The quality of the films prepared can be improved by allowing low-boiling solvents (those boiling below 100°C) to evaporate off at room temperature until no free liquid solvent is evident to the eye. Then the necessary oven and/or vacuum treatment follows. This procedure eliminates the tendency of low-boilers to produce bubbles and uneven surfaces.

To clean a polymer film from a salt plate, usually the same solvent from which the film was cast can be used, followed by an acetone wipe. Occasionally, the polymer remaining on the plate will be found very difficult to dissolve or even insoluble in the solvent from which it was cast. Soaking for several hours immersed in the solvent may clean off the film. Sometimes it proves necessary to polish off the polymer film with a fine abrasive such as double zero emery paper. Acetone is the writer's favorite for cleaning plates. It can be used to clean off many a polymer which is insoluble in it by its swelling action together with hand pressure.

When one wishes to examine a film by the reflectance technique using polymer films, a film-from-solution can be cast on a polished piece of flat metal and the infrared spectrum obtained with a reflection attachment. The effective thickness of the film is thereby doubled, since the beam passes

through the film, is reflected by the polished metal surface, and traverses the film again on its journey to the monochromator.

Pressed Disk Technique

This procedure for preparing solid samples for spectral scanning was introduced simultaneously in Germany by Schiedt,¹⁶ and in the U.S. by Sister Stimson.¹⁷ By using an alkali halide as a matrix for the solid sample, these investigators found they could imbed the sample in a material of comparable refractive index, thus reducing scattering, which also was infrared transparent, and when properly prepared visually transparent, thus giving evidence of adequate preparation.

A milligram (more or less) of sample is ground and mixed with, say, 300 mg of high purity alkali halide (KBr is most widely used), placed in a die, preferably cone-shaped, evacuated to remove entrapped air, pressed at 23,000 psi while under evacuation, to yield a transparent pellet or disk about 13 mm in diameter and 1 mm thick (for one specific type of die).

Lack of evacuation to remove entrapped air soon shows up as a pellet which will become visually opaque in a short time, even when stored in a dry atmosphere.

While the pressed halide disk technique yields an infrared spectrum of a solid sample free of interfering absorptions, extreme care and extensive precautions must be followed to eliminate water absorptions arising from the moisture readily picked up by the hygroscopic halides required. In fact, in the usual infrared laboratory "the game is not worth the candle." Rather than attempt to eliminate these water absorptions entirely, most spectroscopists keep them of low intensity by keeping their powder (KBr or KI) dry, and learn to live with them. For some problems, of course, the two principal regions where water absorbs near 3 and 6.1μ are of no concern. For many problems, they are of interest, and this factor represents one of the disadvantages of the pressed disk procedure. The ideal matrix material for the pressed disk technique has not yet been found. Wanted is one with the other qualities of KBr but without its hygroscopicity.

Both the pressed disk and oil mull techniques yield excellent spectra of solid materials when properly employed. For the general run of solids encountered, the oil mull technique requires less time in sample preparation. Both Nujol and HCBD mull spectra can be run on a solid sample more quickly than a single KBr disk spectrum, including total sample preparation time. The KBr pellet procedure, however, perhaps requires less physical effort on the part of the spectroscopist, and the technique involved is simpler. The biggest single advantage of the pressed disk over the oil mull is the ability to carry out quantitative work directly with the disk technique. While quantitative accuracy is not as high as in quantitative work in solu-

tion, it is satisfactory for many purposes. For qualitative work, however, the oil mull technique has fewer disadvantages than the pressed disk one.

There are now dies of various capacities and sizes offered by infrared suppliers, including micro-dies (see Chapter 16), for preparing pressed disks.

For best disk preparation, the sample should first of all be as finely divided and as uniform particle size as possible. The use of vibration-type mills provides better and faster sample grinding than do manual procedures. Either the solenoid type vibrator developed by Dr. Schiedt or a commercially available dental accessory, the "Wig-L-Bug," are recommended. Addition of volatile solvents during grinding operations is sometimes helpful.

Concentrations of sample to KBr in the range of 0.1 to 0.5% normally yield satisfactory spectra. With an unknown, a good trial concentration is 1 mg of sample to 299 mg KBr for a 300 mg total mix. Depending on the intensity of the spectrum obtained, the concentration can then be adjusted downward or upward as required. If a more intense spectrum is indicated, it is preferable to increase disk thickness by using larger quantities of sample-alkali halide mixture, rather than increasing the concentration of sample in KBr. Otherwise, for higher concentrations, it becomes difficult to produce clear disks. With a 0.33% sample concentration, 1 mg sample plus 299 mg KBr in a 13 mm diameter die, a disk of about 1 mm thickness is produced.

A conical-shaped die has performed best in the writer's experience. A split-cone makes for ready removal of the pellet, and evacuation is necessary to yield consistently clear and reproducible disks. Although unevacuable dies have been used, they will not produce permanently clear disks. An unevacuable die may produce a reasonably clear disk, immediately after removal, but this will gradually change and become translucent as the entrapped air slowly reappears after pressure release. This is undesirable from both qualitative and quantitative standpoints, since absorption and radiation scattering become a function of the time lapse between pressing and recording of the spectrum.

After placing the ground sample-KBr mixture into the die atop the bottom plunger, the top plunger should be inserted and the mix tamped down with rotatory hand pressure. This operation prevents loss of mix when evacuation is begun. The assembled die is then placed in a hydraulic press, the top platen lowered, and slight pressure applied to insure proper sealing of the inside of the die by the rubber gaskets. The die is now evacuated for two minutes after pumping has removed the initial entrapped air, using an ordinary laboratory vacuum pump. Pressure of 23,000 lb total load is applied for a two-minute period while the vacuum is maintained. While some samples can be pelleted with less pressure, few will require more. It is convenient to standardize the procedure by using the same pressure

for all samples, to the extent possible. Care should be exercised not to exceed the safe upper pressure limit for the die stipulated by the manufacturer.

With the vacuum pump running, the pressure tubing is *slowly* removed from the vacuum port, to prevent cracking of the finished disk. The disk is then removed from the die, inserted in an appropriate holder, and scanned in the infrared. It is desirable to position the disk for scanning at the focus of the infrared beam. Adaptors are available from instrument suppliers for this purpose. The disk location becomes particularly critical when micro-size disks are scanned. For these, beam condensers are essential.

The vacuum required in disk preparation doesn't have to be better than a few mm. Any commercial hydraulic press capable of delivering 25,000 lb total load is sufficient. Only high purity alkali halides should be used. Several suppliers offer high purity KBr, e.g., already ground and dried, ready for disk preparation. It is wise to check the purity of each new bottle or batch of KBr by preparing a 2 mm "blank" disk using KBr only. When possible, the KBr should be kept at 110°C in a vacuum oven for storage. When kept in and used from a desiccator, KBr should be dried at 110°C overnight at regular intervals to keep the moisture content as low as possible.

The pressed disk technique has certain advantages over the mull method: quantitative analysis can be done directly on the disk, since its thickness is readily measured; KBr, KI, and KCl have no absorptions in the 2 to 25 μ (5000 to 400 cm^{-1}) region; a number of materials, such as many elastomers or plastics, can be ground with alkali halides, but milled only poorly.

The pressed disk method has several disadvantages as compared to the mull technique: the O-H and N-H str regions are mostly obscured by the O-H absorption of water normally present in the hygroscopic halides; the C-C and C-N region is partially obscured by the 6.1 μ water absorption; polymorphic changes are more frequent in disk preparation than with mulling; the alkali halides are more chemically reactive than mulling agents and halide exchange and other reactions may occur; a mull preparation can be adjusted at any point in the operation, or thickness adjusted after only a portion of a spectrum has been scanned, while the end result obtainable from disk preparation is not known until the disk is removed from the die or until the spectrum has been scanned. If the size disk prepared is at least double the beam area, however, it can be cut in two and scanned at double thickness, avoiding preparation of a new disk, in those instances when the initial scan is not intense enough.

One of the most useful aspects of the pressed halide disk technique is the possibility of obtaining a qualitative identification of a total unknown

from 1 mg down to 20 micrograms of sample. Mulling such a small-sized sample is practically impossible.

Pyrolysis

Hausdorff⁴ suggested and Harms³ developed and systematized a very useful sample preparation technique for those polymeric materials which are so intractable they can not be readily sampled or sampled at all by any other solid state procedure. Examples of this class of materials are certain epoxy resins, "Teflon," "Kel-F," "Dacron," "Terylene," vulcanized rubber, thermosets in general, and molded and baked resins and enamels.

Harms found such intractable polymers may be readily characterized by pyrolysis, followed by examination of the infrared spectrum of the pyrolyzate. One might expect to obtain a poorly defined and featureless spectrum, since the yield of pyrolysis products from a given polymer is doubtless very complex in many cases. Yet, remarkably discrete spectra are the rule rather than the exception. In some instances the spectrum obtained closely resembles the unformulated and uncured or low molecular weight counterpart of the high polymer. This similarity arises from the fact that a number of linear homopolymers crack or pyrolyze into simple monomeric or low molecular weight components. Changes in molecular weight of a given linear polymeric type do not alter the infrared spectrum substantially.

In the pyrolysis procedure the sample size may vary from 2 g to a few hundred milligrams, depending on whether the sample material is estimated to contain a large concentration of inert filler or is 100% polymer. Small fragments of the material of the estimated quantity are placed, e.g., in a 15 by 120 mm borosilicate glass test tube. The tube is held nearly horizontal and heated at its closed end over the inner blue cone of a Bunsen burner flame to 375° to 750°C. The temperature at which pyrolysis occurs depends upon the type of sample. "Kel-F" requires 250° to 500°C, while "Teflon" requires 550° to 585°C, e.g. Heat should be applied as rapidly as possible to minimize charring. The vaporous pyrolyzate condenses to the liquid state on the cooler portion of the tube and is transferred directly to a salt plate through use of a stirring rod or spatula. A sandwich is then made by pressing a second salt plate over a few drops of the pyrolyzate on the first plate and squeezing out to the desired film thickness. The spectrum of the condensed, cooled pyrolyzate is then scanned.

An experienced operator can sometimes make an identification in 20 min total elapsed time, using the pyrolysis technique. For speed at low cost, this procedure has a big advantage over the somewhat more laborious and detailed methods of mass spectrometry.

As the spectroscopist's experience with pyrolysis accumulates, he will be able to recognize a number of polymeric materials from the odors, color changes, and pyrolyzate consistencies, etc. developed during the sample

preparation. The characteristic sweetish odor of burning paper with acetic or butyric acid during pyrolysis, e.g., is a clue to the presence of cellulose or cellulose derivatives. The high thermal resistivity of polytetrafluoroethylene is a positive clue to the presence of "Teflon."

Kruse and Wallace⁶ pyrolyzed all samples under the same controlled conditions into CCl_4 . An aluminum cylinder 3.5 by 1.5 in. in diameter was drilled to a depth of 2.75 in. to accommodate a 15 by 100 mm test tube fitted with a 4 mm glass inverted U delivery arm. A potentiometer, with the thermocouple in a 3/32 in. hole parallel and close to the test tube well, served to measure the temperature of the heating block.

The block attains and holds temperatures in the range of 830°-870°F, using a hot blue Bunsen burner flame. The tube, containing 1 g of the shredded or cubed sample, is then inserted in the well. When decomposition products begin to issue from the delivery arm, it is immersed in 1 ml of CCl_4 . The pyrolysis is best carried out in a hood to personally avoid acrid and unpleasant products. For most elastomers and plastics, 2 min produces a solution sufficiently concentrated for identification. It is wise to be certain some liquid products are collected. The solution is dried by filtering through a column of anhydrous sodium sulfate protected with a calcium chloride drying tube, and then allowed to stand over anhydrous sodium sulfate. The infrared spectrum of the products collected is then scanned vs CCl_4 to compensate for the solvent.

The Kruse and Wallace procedure favors close reproduction of spectra by pyrolyzing all samples under the same controlled conditions, and minimizes fogging of salt windows by moisture present in the pyrolyzates. The solubility of pyrolysis products in CCl_4 poses a problem. Out of more than 100 pyrolyzates, however, these investigators found only two—pyrolyzates from urea and urea-melamine plastics—where not enough solute was present to yield a characterizing spectrum.

Pyrolyzate spectra can only be safely compared against known *pyrolyzate* spectra, since there are spectral differences, sometimes slight, as compared to spectra obtained by much less drastic thermal treatment of samples. It is then necessary for the spectroscopist to augment the fine spectral collection of Harms by scanning his own known pyrolyzates. The paper by Harms should be consulted for further details of the pyrolysis technique.

Pyrolysis is normally only employed as a sample preparation technique when other less drastic solid sampling procedures fail or when speed and a simple generalized identification of an intractable solid is desired.

Miscellaneous Techniques

There are other methods of preparing solids in addition to those described. The technique of *attenuated total reflection* (ATR) is useful to readily obtain characterizing spectra of solid plastics, elastomers, fabrics,

adhesives, powders, foams, and inorganics. A better description of the process involved is *internal reflection*; and *multiple internal reflection (MIR)*, and *frustrated multiple internal reflection (FMIR)* are words recently thrust into the spectroscopist's vocabulary. Samples are cut to size and clamped in position against the internal reflection plate. The incident infrared radiation is reflected from the sample after penetrating to a depth in microns provided the proper angle of incidence, refractive index, and absorption coefficient conditions are met. Internal reflection spectroscopy is presented in detail in Chapter 15.

Several literature articles have appeared over the years, describing solid sample preparation by depositing particulate solids directly onto a salt window. Investigators have also brushed them on in solution or slurry form and eliminated the solvent or dispersion medium by normal evaporation or by rapid heating starting with prewarmed windows.

Hunt, Wisherd, and Bonham⁵ presented a very useful collection of 68 spectra of minerals, rocks, and inorganic chemicals. They ground about 5 g of sample to a fineness passing a 150-mesh screen. The ground powder is added to 250 ml of distilled water with a small quantity of dispersing agent — 15 ml of 0.2*N* sodium oxalate for clays, and 5 drops of sodium metasilicate for carbonates, silicates, and inorganic chemicals. The mixture is violently agitated in a Waring Blender for about 10 min. The suspension which forms is poured from the blender into a 250 ml graduated cylinder and allowed to stand 2 hr. Then the upper 5 in. of the suspension will contain particles less than 5 μ in diameter. The exact particle size distribution obtained, which can be calculated from Stokes' law, will vary somewhat, depending on the specific gravity of the sample and the temperature. The upper 5 in. (12.5 cm) of suspension are drawn off and centrifuged to separate the sediment from the solution of the dispersing agent. The sediment is dried at 105° to 110°C for 24 hr, and kept in a desiccator prior to use. The oven dried sample is crushed in a small mortar to separate particles which have adhered together, and some of the powder is placed on a sodium chloride window. A few drops of isopropanol are added to form a paste. The paste is smoothed out on the window with a microscope slide whose edges have been beveled and polished to prevent scratching. When the slide is removed, the alcohol evaporates, leaving a thin film of sample on the window. This is placed in the sample beam and scanned vs a blank sodium chloride window in the reference beam. After recording the spectrum, the window with the powder film is weighed before and after removal of the film with alcohol. The difference in weight divided by the area is recorded on the spectrum as milligrams per square centimeter. The window must be handled with rubber finger tips or tongs to prevent it from changing weight.

To better bring out weak absorption bands, when desired, a very thick sample can be scanned, but the over-all transmitted radiation is seriously decreased. To compensate for this, with a double beam instrument, the shutter in front of the reference beam can be lowered; with a single beam instrument, the slits can be opened. These procedures have the effect of increasing the difference between the two beams.

If equipment for very fine grinding is available, it is preferable to grind a small sample completely to particles less than 5μ in diameter. This eliminates sedimenting, centrifuging, and drying to isolate the fine particles.

No matter how a sample is prepared for scanning in some region of the infrared, a window or cell transparent to radiation in that region is required. One of the few exceptions is the scanning of an unsupported film material. Before proceeding to a discussion of sample preparation techniques for liquids and solutions, let us first consider the preparation, use, and care of absorption cells.

PREPARATION, USE, AND CARE OF ABSORPTION CELLS

A wide variety of windows (plates) and absorption cells all ready for use are now commercially available from approximately a dozen suppliers. While initially relatively expensive, with proper care they have a long life-time, which reduces their per spectrum cost to a small figure. Furthermore, cell repair service is widely available at reasonable cost. On the basis of economics alone, it is not worthwhile for the spectroscopist to make or repair his own fixed-thickness or variable-thickness absorption cells. Those who have grown up with the art of cell-making from the early days of infrared probably cannot convince themselves of this fact. It is, however, such a simple matter to polish single salt plates, such as those of NaCl or KBr that every serious spectroscopist should learn the technique. It is good economy, as well as a means of providing some slight physical exercise to an otherwise rather sedentary occupation.

Being able to make and repair one's own cells, however, is advantageous. The ability to design and make special purpose cells which are not available commercially is obviously of great value in giving the investigator more leeway in the problems he can tackle and solve. Moreover, more venture-some experiments can be tried with aplomb when the ability to readily repair a "fogged" or otherwise damaged sealed cell is at hand.

Polishing Alkali Halide Plates

Since the most widely used cell windows are NaCl and KBr, their water solubility presents several problems. Both a single window or a fixed-

thickness cell comprised of two salt plates separated by a spacer material will eventually become "fogged" through use. Enough moisture in the sample, the solubility (though often limited) of water in organic solvents, and high humidity on days when the dehumidifier is out of order, will bring about foggy plates sooner or later, even with scrupulous care. Already cleaved and polished salt plates of almost any specified thickness are available commercially. Many spectroscopists prefer, however, to order salt plates which are cleaved only, in order to prepare the specific sizes they like and give the windows the polish they desire. Occasionally, very thin plates are required, or it may be thrifty to cleave a badly eroded window and reclaim, say, half the thickness instead of repolishing the badly eroded window. It is valuable to learn how to cleave salt plates.

Since NaCl windows are far and away the most commonly used in chemical spectroscopy, discussion will be largely confined to this material. Salt crystals, like others, are split along a cleavage plane, since this is the only way to cut leaving nearly smooth faces. The cleavage planes are those directions in a crystal where there is a minimum of cohesion between the atoms. By chipping a corner of a plate and inspecting it, one can readily determine the direction of the cleavage planes. If the starting material is a cleaved blank, the chances are good that it has been already cut along a cleavage plane with a moistened string. A single-edged razor blade is conveniently used to cut an indentation line with a ruler or the straight edge along the desired line of cut. The same razor blade is then inserted in the crack made and tapped with a small hammer until cleavage occurs. The surfaces produced by cleavage will seldom be perfect and must be flattened by grinding and smoothed by polishing. In the hammer-tapping operation, if not carried out ideally, a bow or bend may develop in the cleaved plates. This is not fatal since this can usually be removed by pressure applied during the grinding operation. It does result, however, in the loss of some expensive salt.

Rocksalt grinds easily; only one grit size is required. Some workers prefer using a slurry of #500 Carborundum in water.¹⁰ This is prepared and placed on a heavy flat glass plate. Several circular and figure-8 strokes serve to grind the salt plate flat. At the conclusion of the grinding operation, the slurry is washed off the plate with acetone.

The writer has successfully used #00 emery paper or even crocus cloth to grind NaCl plates. This is a dry process and requires no slurries. The emery paper should be positioned on a flat immovable surface. The salt plate is simply pushed with a circular and/or figure-8 motion, both clockwise and counterclockwise, over the emery surface, until visual observation shows the surface being ground is uniformly "white." Residual loose salt is wiped from the plate surface with acetone before polishing begins.

The two most widely used methods for polishing ground plates to a smooth, flat finish are the cloth-lap and pitch-lap methods. The majority of spectroscopists use the cloth-lap technique because the preparation and use of a cloth-lap is simpler. The pitch-lap is more tedious to prepare but yields superior results in a shorter time.

Cloth-Lap Method. The lap is built by stretching several layers of a soft, lint-free fabric tightly over a flat, circular, glass plate, conveniently about 10 in. in diameter and $\frac{1}{2}$ to $\frac{3}{4}$ in. thick. The cloth can be cotton diapers or an undyed woolen piece which has been worn smooth. Wool has the advantage of confining water, when it is used for polishing, to a small region of the lap surface. With a cotton fabric this is not easily accomplished. The flat, circular, glass plate can be bonded with a glass-to-metal adhesive to a heavy piece of round scrap steel from any junkyard. It is preferable that the diameter of the "scrap" top be very slightly less than the diameter of the glass plate and that the surface be freed of rust and ground reasonably flat and smooth before the bonding operation.

The wool cloth is held in place by a door spring or one or more heavy duty rubber bands. A small volume of distilled water is placed on the cloth near the edge and confined to an area roughly 2 by 2 in. The first volume used will "sink in"; more water is added, and the excess rubbed off with the fingers several times, until wiping the moist surface with dry fingers reveals only a thin layer of water on the fingers. Polishing is accomplished by quickly moving the salt plate with some downward pressure from a dry area of the cloth surface through the moist area, then quickly moving to a dry area and executing several circular and/or figure-8 motions, alternately clockwise and counterclockwise. The plate will often fog in surface areas near where contact is made with the fingers holding it. Thin rubber gloves or finger cots can be worn to prevent this. A less elegant but effective procedure is to drape small towels over each shoulder, using one for the "dry" finger wipe and the other for the "dry-dry" finger wipe. After a little practice, one is able to polish salt plates without fogging them and without having to wear any protective devices on the fingers. The polishing operation just described may have to be repeated three or four times, depending on one's experience and the precise condition of the surface of the starting material, the already ground salt plate.

Admittedly, the above polishing procedure requires some practice and attention to fine details, or a smooth, flat finish will not result. A safer procedure for the beginner is to use a fine particled (about 5μ average diameter) polishing agent, such as red rouge, alumina, magnesia, titania, or certain rare-earth oxides. Red rouge is successfully used by many. Sprinkle a small quantity of the agent over the cloth lap and wet with a few drops of 95% ethanol. The salt plate to be flattened is then polished

with circular (or figure-8) motions in alternate directions which cover practically the whole surface of plate and cloth. After polishing for roughly 20 or 30 sec, the plate is slid off the lap and quickly wiped dry by rubbing it on a similar lap, which is clean and dry. Or a few layers of cloth on a flat glass plate on the bench will suffice. Flatness is checked by interference fringes whenever the polished salt plates are to be used in the construction of a sealed cell. If polished plates are to be used for cast films or as an unsealed sandwich to hold liquid films or mulls, the eye is normally an adequate judge as to whether the desired flatness has been attained.

To check flatness, the salt plate is placed on a glass optical flat. The work is illuminated with substantially monochromatic light such as emitted from a sodium vapor light. Interference fringe patterns will be observed. The plate should be flat to within a few fringes or repolished until such degree of flatness is obtained.

Pitch-Lap Method. A pitch-lap is a circular array of flat squares of optical pitch, separated from one another by a narrow air space, adhered to a circular metal block. Potts¹¹ gives details for preparing a convenient-sized pitch-lap, including construction of the mold.

Since this type lap becomes either slightly convex or concave through use, it must be made flat at regular intervals. This can be done by flooding the working surface with a very dilute suspension of any of the polishing agents given above for the cloth-lap. A heavy slab of flat glass, which has been warmed slightly, is then placed over the working surface. Additional weight is placed on the glass so that the total weight on the pitch-lap is about 8 to 10 lb. Under the steady pressure, the pitch flows slowly and the lap begins to flatten. Acceptable flatness is reached when the raised squares of the pitch-lap show uniform bright black through the glass slab. The grooves will be white if, e.g., a white polishing agent is used. The glass is removed, the slurry washed off, and the lap is ready for immediate use.

A watery (and not the least pasty) slurry of polishing agent in small quantity is put on the lap. This can easily be accomplished by dipping the fingers in water, then lightly in polishing powder, followed by spreading over the pitch-lap surface.

The salt plate requiring polishing is held in the fingers, protected by rubber gloves or finger cots, and pushed over the lap surface, covering it uniformly and entirely with a systematic circular motion. Initially the water begins to dissolve the salt plate surface and levels it quickly. Rather soon the polishing slurry becomes saturated with salt and the cutting action ceases. The plate is speedily slipped off the lap and dried by rubbing it quickly and rather vigorously on several layers of soft cloth laid out on a flat surface. A very high luster is produced on the salt plate surface by this technique.

The pitch-lap can be conveniently stored in a refrigerator or icebox near 0°C, for if left at room temperature too long, the pitch will flow and lose its shape. Following each use, the lap is rinsed well with cold water before storage. Otherwise, the residual polishing agent is removed only with great difficulty.

Halides Other than NaCl. Potassium bromide is softer, more water soluble, and is worked up faster in all operations than NaCl. KBr plates, however, can be cleaved, ground and polished using the same procedures as for NaCl.

CsBr and CsI are most easily polished by the cloth-lap technique because of their high water solubility. Owing to this high water solubility, they fog very easily and high luster plates are difficult to prepare. Since these materials are used at long wavelengths, fogginess and low luster surfaces are readily tolerated. Small surface irregularities will normally be less than 20μ in size, so radiation scattered thereby will not be "seen" in their 20 to 50μ range of greatest use.

LiF, CaF_2 and BaF_2 cleave more easily than NaCl or KBr, owing to their greater hardness. This greater hardness necessitates their being ground with successively finer abrasive grits. For example, #500 Carborundum can be used for rough grinding and #600 Aloxite for fine grinding. CaF_2 and BaF_2 are practically insoluble in water and therefore can be used as plates in the preparation of cells for aqueous solution studies. The Dow Chemical group¹² has found that concentrated HCl solution (12*N*) can be successfully used as the suspending fluid for the polishing agent in the pitch-lap technique of polishing these three fluoride materials. The normal precautions in handling concentrated HCl should be observed.

Silver chloride is so soft it is not normally cleaved, ground, or polished. It is supplied with sufficient luster and flatness so that polishing is not necessary. A technique for refurbishing a damaged (scratched, etc.) surface of a AgCl plate is available from suppliers, but it is too tedious and uneconomical for a spectroscopist. This material can be purchased in approximately 1 mm thickness sheets and these are readily cut to size with sharp scissors. AgCl darkens (purple to eventual black) upon continued exposure to visible and ultraviolet light and therefore should be stored in a light tight container. It also naturally reacts with any metal higher than silver in the electromotive table and forms the chloride of the metal with which it is in contact. Accordingly, AgCl plates or disks should not be left in a stainless steel, e.g., cell any longer than necessary. The hygroscopic metal chlorides formed produce a mess, disfiguring both the metal plates and the AgCl. Owing to its extreme softness, silver chloride is not ordinarily used for windows in permanently assembled cells, only in demountable ones.

Cell Construction and Repair

High quality absorption cells of practically any type for which there is reasonable demand and polished NaCl and other infrared window plates are available commercially from firms which manufacture infrared instruments and from those which specialize in optical materials. Most of these companies also repair damaged cells and plates or apply their residual value towards the purchase of new ones. The cost of the above parts and services is less than the cost for a spectroscopist to make and repair his own cells. During the course of oil mull, cast film, and capillary film scanning of spectra using salt plates in demountable cells, however, a continuing need arises to repolish fogged, scratched, and otherwise disfigured plates. Everyone who uses infrared more than casually, therefore, should learn how to grind and polish NaCl plates at least. This will save considerable expense, as adequately cared for plates can last a long time and provide for the scanning of a large number of samples.

For those interested in building their own cells, the techniques required are not difficult and have been adequately described.^{7,11}

A scientist employed by a large industrial, academic, or government institution may have access to an optical shop or laboratory which can build cells for him and repair them as well. If he does not, he can rely on suppliers to both build and repair his cells; he may buy fixed-thickness and the more complex cells, but repolish the plates of demountable cells; or he may rely, at least partially, on expendable cells. One type of the latter is the cavity cell made by ultrasonic machining; another is the expendable type made, e.g., of AgCl with inexpensive plastic backing plates. The low cost of these makes it practical to use them only once, or a few times, then discard them.

The cell windows most often used in infrared spectroscopy are water soluble, relatively soft, and easily scratched. Special precautions are needed for proper cell care (Chapter 6).

LIQUIDS AND SOLUTIONS

Liquids

A liquid of low volatility can most readily be scanned for qualitative purposes by placing a drop between rocksalt plates which are squeezed together, held in an appropriate holder, and inserted in the sampling space of the spectrophotometer. When no spacer is placed between the salt plates, the thickness is generally designated "capillary" thickness. For liquids boiling below about 70°C, a sealed cell is required. Otherwise the "capillary" thickness film will have at least partially evaporated before completion of the scan.

If a capillary thickness scan of a liquid does not produce an intense enough spectrum, it is convenient to place a 0.005 in. thickness of Nichrome wire between the salt plates just outside the area seen by the infrared beam. This increased film thickness often produces the desired spectral intensity. The technique is easy, fast, and no significant distortion of the spectrum results.

With a few liquids even a capillary thickness will produce too intense a spectrum in certain spectral regions. Solution in a solvent having a window in the region of interest should then be resorted to.

Solutions

Scanning infrared spectra in dilute solution has the significant advantages of yielding reproducible spectra because the molecular surroundings are always the same and of providing for the carrying out of both qualitative and quantitative analysis on the same scan. Potts and Moss in Chapter 6 discuss solution spectra, the advantages of the $\text{CCl}_4\text{-CS}_2$ solvent technique, and the most useful other solvents.

The limitations of solution spectra are imposed by a lack of solubility in a solvent or solvent combination or by solubility only in a solvent which itself possesses a complex absorption spectrum. Any organic solvent will suffice for solution spectra provided it has a window in the spectral region of the spectroscopist's interest. Again, it must be emphasized that spectral comparisons for valid spectra-molecular structure correlations should only be made on spectra in the same solvent at equivalent concentrations.

Aqueous Solutions. Aqueous solutions are normally avoided in the infrared, since water is a strong absorber, the more expensive water-insoluble materials must be used for cell construction, and considerable limitation is placed on the concentrations that can be employed dictated by the limited thicknesses of cells permissible. Moreover, the effective spectral range for water solution work is limited to the 6.5 to 10.5 μ region.

Many materials, however, are soluble only in water. And many biological systems can only be studied in aqueous surroundings. Otherwise their study would have no valid meaning. The examination of biological fluids by infrared has become important and will soon become a major clinical and pathological tool. Chapter 2 discusses infrared techniques in aqueous solution.

Samples Containing Water. While water is best eliminated or reduced below 1% by weight from a sample before scanning in the infrared, when necessary or desirable, satisfactory spectra can be obtained from liquids and solids containing as much as 20% by weight water. The NaCl plates used will require repolishing after such scans, so sealed cells should not be used. How high a concentration of water can be tolerated depends upon

how strongly the water is hydrogen-bonded to the sample. The stronger the hydrogen bonding, the higher the concentration of water that can be tolerated. The spectrum obtained, of course, will be complicated by the presence of water absorptions so that the 3μ region will be of no use for observing sample absorptions. Some interference will also be produced by the 6.1μ water band and in the 4 to 5μ region. This latter region is often not of interest.

Compensated or Differential Scanning

In a double-beam spectrophotometer, absorption common to both beams will not be seen in the recorded spectrum. The advantages this brings in eliminating solvent absorptions from a spectrum by scanning with solvent only in the reference beam is discussed in Chapter 6.

Differential scanning, as it is called, is not limited to cancelling out solvent absorptions. It can be applied to solid, liquid, and gaseous state samples. In qualitative work it is usually not desirable, nor worth the effort, to effect complete cancellation of absorptions by selected components. Generally, it will be found most satisfactory to have a very slightly higher concentration of the component to be cancelled out in the sample beam as compared to that in the reference beam. Variable thickness cells are available from several manufacturers of infrared instruments and/or accessories. These make it relatively easy to cancel out absorptions, to the extent desired, in differential scanning.

Particular caution should be applied in the interpretation of compensated spectra. In regions below 10% transmission, a compensated spectrum is suspect and often meaningless, because the instrument must "see" a certain minimum amount of infrared to operate effectively. Otherwise the spectrophotometer is "dead" and the recording in that region of no validity.

VAPORS

The spectra of gaseous samples can be conveniently obtained in glass or metal tubes, the ends of which comprise infrared transparent windows attached with a cement, such as Glyptal, Apiezon wax, paraffin wax, or other sealant impervious to and nonreactive with the samples. It is advantageous to provide legs on the gas cell, so when placed in the spectrophotometer sampling space it stands at the proper height for immediate scanning.

For the vapor samples most commonly encountered, a 10 cm path length cell is sufficient. Either the gas pressure, the cell length, or both may be adjusted to give the desired intensity of absorption. Gas pressures required may run from 5 mm or even less for strongly absorbing substances like fluorocarbons, to $\frac{1}{2}$ atmosphere for weak absorbers such as hydrogen

chloride or water vapor. While gas cells in general use vary from 5 cm to 30 cm in length, there are occasional requirements for 2 cm, 1 m, 10 m, and even 40 m cells. In air pollution work and in breath analysis, 10 m and 40 m path length cells are used to identify and determine components in the ppm and ppb ranges.

It is more satisfactory for a vapor cell to have separate entrance and exit ports, but one port serving both functions is sufficient. Normally, cells are filled by first evacuating them and then drawing in the sample to the desired pressure. A system for handling gas sampling should include a pressure gage, sample inlet, vacuum pump, and absorption cell ports. Since the intensity of the rotation-vibration bands observed for a gas is a function of both the partial pressure of the absorbing gas and the total gas pressure, it is desirable to include an inlet port for a pressuring gas in the system. By pressuring a gas sample to convenient total pressure with a nonreactive, nonabsorbing gas such as nitrogen or argon, quantitative analysis can be done in the vapor phase. In the absence of constant total pressure, intensity and band half-width comparisons amongst gas samples will be meaningless. For qualitative work, pressuring to constant total pressure is not necessary but facilitates identifications.

Most commercial spectrophotometers have only somewhat more than 10 cm length of sampling space. Therefore, gas cells longer than 10 cm are of the multiple reflection type.

Water vapor has a considerable number of obscuring infrared absorptions. It is well, therefore, to first dry a gas sample which is not reasonably free of water vapor, before scanning.

A gas cell with separate entrance and exit ports can be filled by flushing, when the spectroscopist is not sample limited.

It is convenient to construct a gas cell with a short sidearm projecting from the cell body. Thereby a small amount of sample can be frozen out and later expanded into the cell chamber.

The spectra of gases at high pressures and high temperatures has become more important in recent years for both theoretical and commercial investigations. Absolute intensity measurements at pressures in the 100 atmosphere range have been used for theoretical work. At such pressures the individual rotation lines of a vibration-rotation band broaden to the extent that the entire band envelope becomes an absorption continuum. This makes accurate absolute intensity measurements feasible. Gas cells for high pressure and high temperature work must be of special design to withstand the conditions imposed. One great difficulty is finding infrared transparent cell windows which will withstand the high pressures.

With ingenuity, the investigator can discover ways in which gas phase spectra will be helpful, other than for the usual qualitative and quantitative analysis of gaseous samples. A liquid formulation, e.g., may contain both

volatiles and nonvolatiles. Some separation of components may be effected by drawing the volatiles into a gas cell and scanning. This will simplify the identification of the total components of the formulation.

Mass spectroscopy and vapor phase chromatography (VPC) have supplanted infrared for the qualitative and quantitative analysis of light gases, particularly in routine work where the individual components likely to be present are pretty well known. VPC is strong on component separation but weak on component identification. It therefore nicely complements infrared spectroscopy. The marriage of the two increases the power of both tools.

FILMS

If a self-supporting film of a sample is available in a thickness yielding an optimum intensity spectrum, it can be scanned as-is, either unsupported directly in the infrared beam or between salt plates. With the thin films required, interference fringes often are observed in the spectra thus recorded, owing to the interference of infrared rays reflected at the front and back surfaces of the films. These normally undesired additions to a spectrum can be a nuisance particularly, e.g., in identification of a terpolymer when one of the co-monomers is present in low percentage. Such interference fringes can be eliminated or greatly reduced by smearing a thin film of Nujol on the film surfaces. This technique introduces Nujol absorptions into the spectrum, but the regions of Nujol absorption can be rescanned after smearing another section of the film with hexachlorobutadiene or perfluorokerosene (or the Nujol may be removed from the same specimen of the film and the HCBd or PFK added).

Film materials of too great thickness for as-is scanning can be prepared for scanning by the film-from-solution technique, when solvents for them can be found. For insoluble film-forming materials, some can be mechanically pressed using pressure and/or heat to yield films of satisfactory thickness and quality for infrared scanning. Others may be amenable to microtoming. When satisfactory films can be prepared by the above procedures, they provide for rapid qualitative and reasonable quantitative analytical procedures. This is particularly true for plant quality control requirements, and for analytical research service where, e.g., minor changes in monomer incorporation into a copolymer are being evaluated.

SPECIAL SAMPLING TECHNIQUES

Attenuated Total Reflection

In the last few years interest in reflection spectra has been revived by the introduction of a useful technique of attenuated internal reflection by

Fahrenfort.² This technique is popularly known as ATR (attenuated total reflection).

An infrared spectrum obtained by direct reflection from the surface of an organic substance is usually of poor intensity and quality. The reflected intensity is a complex function of the angle of radiation incidence, the refractive index, and the absorption coefficient. When the phase contiguous to the reflecting surface is a medium of high refractive index, total reflection, attenuated as a function of the absorption coefficient, can be produced. By using such materials as AgCl or KRS-5 hemicylinders or prisms as the contiguous phase, therefore, useful reflection spectra can be obtained.

Since the reflection intensity resulting is a function of the angle of radiation incidence and is independent of the thickness of the reflecting material, several useful applications of ATR become possible. The ATR technique and its applications are discussed in Chapter 15.

Polarized Infrared

Orientation of chemical groups in single crystals of substances and in polymeric films and fibers can be determined through use of polarized infrared radiation. One of the criteria that must be met for the absorption of radiation is that the vector direction of dipole moment change and the direction of the electric field component of the incident radiation be the same. When the molecules of a sample are randomly oriented and irradiated by an ordinary infrared beam, the electric field directions of the radiation are also randomly oriented. No spectral differences will be observed, therefore, as between a spectrum scanned on such a sample in a given position and one scanned upon rotating the sample 90°. When the molecules of a sample are oriented, however, and irradiated by a polarized infrared beam, the situation is different. Now the intensity of certain absorption bands observed will be different as between a scan in a given position and the one obtained upon rotating the sample 90°. If a specific absorption band is found to be more intense in the first orientation than the second, then the orientation of the chemical groups giving rise to this absorption is such that the vector direction of dipole moment change and the direction of the electric field component of the radiation are largely parallel. When a specific absorption band is found to be more intense in the second orientation than the first, then the directions of dipole moment vector and radiation electric field component are largely perpendicular. No difference in intensity between the two orientations, of course, indicates a random orientation for the chemical grouping concerned.

Caution is required in making chemical structural deductions from such measured dichroic ratios as described above. The chemical bond direction in a molecule may or may not be simply related to the vector direction of the dipole moment change.

Polarizers for infrared radiation are based on the principle that a ray reflected from a surface cannot be reflected in a direction that is colinear with its electric vector. Thus by arranging a number of plates of a material of proper refractive index in the infrared beam at a certain angle, the horizontal component will be transmitted practically unchanged, while the vertical component will be diminished by reflection loss to a low value. Horizontally polarized light of high purity results.

The "certain angle" is the Brewsterian angle, and equals $\arctan n$, where n is the refractive index. For AgCl the Brewsterian angle is 63.5° .

A simple polarizer can be constructed using a series of five AgCl plates as described by Potts.¹⁴ The sample under examination is mounted so that it can be rotated with respect to the polarizer. Since polarization effects are characteristic of infrared spectrophotometers, most particularly grating instruments, it is not wise to keep the sample fixed and rotate the polarizer. Infrared polarizers are available commercially from instrument and accessory manufacturers.

Heated Cells

For some purposes spectra are occasionally required at temperatures above room temperature. Phase transitions between the different crystalline forms of an organic chemical may require investigation. Quantitative work on a copolymer which is a mixture of crystalline and amorphous forms at room temperature may be the objective. When examined in the molten state at higher temperature the copolymer will be amorphous and the complicating factor of spectral differences arising from varying crystalline/amorphous ratios eliminated. Conversely, the percentage crystallinity of a crystalline-amorphous polymer may be desired. Comparison of spectra at room temperature and at elevated temperature in the molten state will reveal which absorptions are characteristic of crystallinity and which characteristic of the amorphous state.

In polyethylene, e.g., the weak 1900 cm^{-1} absorption can be used to determine crystallinity if a polymer of known percentage crystallinity is available for a standard. A 1305 cm^{-1} absorption is unique to the amorphous form of polyethylene. Using the ratio of its base-line absorbance at room temperature to that in the molten state yields the amorphous content at room temperature and the crystallinity by difference. With polyethylene, as with other polymeric materials, care should be taken not to scan the spectra in the molten state too soon after the onset of the liquidus condition. It requires some time for the 100% amorphous state to be realized. One should determine this time requirement experimentally. For polyethylene, a lapse of 15 min after the onset of liquidity is recommended before spectral scanning.

Heated cells are available commercially or the investigator may wish to design and/or build his own heated cell. This can be readily done. A Bakelite plate with a hole-handle for easy entrance and removal is made to fit the sampling space grooves of the spectrophotometer. Two aluminum heat baffles are mounted parallel to the Bakelite plate and separated from it and each other by about $\frac{1}{4}$ in. thickness of insulating material. Then comes the aluminum fore- and copper back- plates to hold the NaCl or KBr windows. The back-plate is separated from the second aluminum baffle by another $\frac{1}{4}$ in. of insulation. Three rods, anchored to the Bakelite plate, project through the two baffles and are attached to the copper back-plate, forming a rigid assembly. Three threaded rods, anchored to the copper back-plates, project through appropriate holes in the aluminum fore-plate and the salt plates are held together between the metal plates with spring-loaded knurled nuts. The copper back-plate has forward projecting arms at a 45° angle from both sides of either end. Between each of these is a Nichrome wire assembly connected to a 110 volt AC circuit via a rheostat. Each resistance wire assembly is covered with steampipe insulation. By controlled electrical input, the copper back-plate is heated and heats the salt plates with which it is in contact. Care must be taken, of course, to lower and raise the temperature of salt plates slowly. Suitable holes are obviously made in all the plastic and metal plates of the assembly to allow passage of the infrared radiation. The cell described has been used successfully up to 200°C . More elaborate and elegant designs for heated cells are available in such journals as the *Review of Scientific Instruments*.

Low Temperature Cells

Since the distribution of intensity among rotational bands in molecular spectra is strongly temperature dependent, the variation of intensity with temperature can often be used for confirmation or rejection of a given analysis of a band system. An infrared absorption spectrum can sometimes be considerably simplified if it is obtained at liquid-nitrogen or liquid-helium temperatures. The study of rotational isomerism is aided by low temperature spectra. At low temperature, e.g., the low energy rotation isomer will be favored and the absorption intensity of the higher energy rotation isomer will be reduced, as compared to their spectra at room temperature.

Low temperature cells are usually constructed on the basis of a demountable Dewar with the infrared cell inside the evacuated space near the lower extremity, windows being provided in the outer wall to allow radiation passage. Any salt windows that are exposed to the surrounding atmosphere must be near room temperature or rapid condensation of moisture will occur, resulting in damage to the salt plates and transmission loss.

An inherent instrumental difficulty is encountered in the use of an optical-null double-beam spectrophotometer for low temperature spectroscopy. A cold specimen in the sample beam is being compared with a room temperature reference-beam attenuator. The latter radiates more energy to the detector. In regions of near total absorption by the sample, this extra energy drives the recording pen below 0% transmission, particularly at low frequencies, because blackbody radiation from the attenuator there becomes a larger fraction of the radiation from the high temperature infrared source.

Typical designs of useful low temperature cells are those of Willis and Miller¹⁸ and Crawford *et al.*¹⁵

Surface Adsorption Apparatus

The spectra of molecules physically adsorbed or chemically adsorbed (chemisorption) on surfaces is of great interest particularly to those concerned with catalytic reactions (see Chapter 2). A specific surface catalyzes a chemical reaction because the molecules adsorbed on that surface have been altered in the course of adsorption making them more reactive. If the spectrum of the molecules can be obtained while in the adsorbed condition, much information can be learned about the effect that various surfaces have on different molecules.

In essence, infrared spectra of adsorbed molecules are obtained by passing source radiation through a catalyst bed, a thin layer supported on a surface transparent to infrared radiation with the molecule of interest adsorbed on the catalyst surface at one monolayer thickness, and into the spectrophotometer. The experimental technique and apparatus required is not simple.

Fine particle silica ("Cab-O-Sil," e.g.) is often chosen as the catalyst support, since in thin layers it is transparent to about 5μ (2000 cm^{-1}) and produces a large surface area. A slurry of this silica in an aqueous solution of the catalyst metal (salt form) is dried, and the powder pressed into a thin layer on a CaF_2 plate. The catalyst layer is then heated in vacuo to 200° to 350°C and reduced with hydrogen. The metal particles supported on the silica are prepared to be less than a few hundredths of a micron in diameter, and the metal should represent about 5 to 10% by weight of the catalyst bed. The catalyst is now degassed at elevated temperature, cooled to the temperature of the adsorption study, and the gas molecules admitted until the desired thickness has been adsorbed on the catalyst surface. The spectrum of the adsorbed molecules is then scanned.

The intricate apparatus required for adsorption studies in the infrared is beyond the scope of this book. Interested investigators should consult the details of the apparatus and the techniques as given, e.g., by Eischens and Pliskin¹ and McDonald.⁸

Micro-techniques

When the sample is limited, micro-techniques must be used. A wide variety of microcells are available for gas, liquid, and solid samples, both from instrument and accessory manufacturers, and from designs reported in the literature. A typical gas microcell provides minimum volume and path length by making use of multiple reflections and careful design. Liquid microcells are normally filled through the capillary action provided by a small-diameter, attached, hollow "needle," or through use of a Hamilton syringe, the type widely used to deliver microliter volumes in VPC. Microcells can be used for both mulls of solids and alkali halide pellets. With most commercial instruments it is necessary to use beam condensers (see Chapter 3) when scanning the spectrum of a micro-mull or a micro-alkali halide pellet. These are either of the reflecting or refractory type.

The reader is referred to Chapter 16 for discussion of the techniques and applications of micro-sampling.

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A General Procedure for Qualitative Interpretation of Infrared Spectra

David N. Kendall

The infrared spectrum has been scanned. Here is the recorded graph of per cent transmittance vs wave number (wavelength). What does it mean? To the novice this confrontation may be a bewildering experience. How does one go about interpreting this spectrum? To the veteran spectroscopist, interpreting spectra is second nature, but even the experienced worker has misgivings until he has unfolded either the maximum amount of information available in the spectrum and convinced himself his findings are correct, or until he has answered the question(s) he sought to answer by running the spectrum.

This chapter presents a general procedure for the qualitative interpretation of infrared spectra. It is hoped the procedure given will smooth the path for the beginner and possibly also provide some new or different approaches to spectral interpretation for the experienced spectroscopist.

VALUE OF SAMPLE HISTORY

Sample history is a vital prelude to spectral interpretation. The more the interpreter knows about the sample, the more quickly and more successfully can the spectrum be interpreted. Should an unknown give no ash, e.g., usually the possible presence of inorganic materials need not be considered. When the sample is a food product, arsenic derivatives, lead salts, and the like can normally be removed from consideration. If the sample is water insoluble, the interpretation can't be correct should it reveal the presence of a water soluble substance.

Throughout the qualitative interpretation of the spectrum of an unknown, all available information about the unknown should be borne in mind and applied. While the investigator sometimes will be confronted with an unknown on which there is no useful sample history, normally a considerable body of information is available on an unknown before the spectrum is scanned. Many times the investigator should use his initiative and find out as much as he can about the sample history, particularly when he has been given no or incomplete sample history. Chemists unfamiliar with infrared spectroscopy may not realize how valuable the sample history can be to facilitating an accurate identification or interpretation of a spectrum.

The following information is valuable: the chemical elements known to be present, the chemical elements known to be absent, the physical state and color, the purity of the unknown -- whether a single compound or mixture, its end use, and component(s) possibly present. The value of the above information should be obvious. If the unknown is red in color, e.g., then the identification cannot be correct if the result is a white substance. Whether an unknown is a single substance or a mixture of materials is certainly of great importance. If the investigator is identifying a "single compound," when in reality he is confronted by the spectrum of a mixture, obviously confusion and error will result.

Time spent by the spectroscopist in obtaining a very thorough sample history will be very well spent in reducing the interpretation time required for answering the questions asked about the sample.

SPECTRAL INTERPRETATION PROCEDURE

The interpretation procedure given here covers the 5000 to 667 cm^{-1} (2 to 15μ) region. An analogous approach can be applied to other regions of the infrared with appropriate modifications. In general, far fewer substances have had their spectra scanned in the region beyond 15μ . While some spectra-structure correlations have been made particularly in the 15 to 25μ region, and a few out to 50μ , the number of such correlations is still relatively small compared to those already made in the 2 to 15μ region. Very much extensive and intensive "spade work" yet needs to be done in the matter of spectra-structure correlations in the region between 15 and 50μ (667 to 200 cm^{-1}).

The first step is to divide the rocksalt infrared into its characteristic functional group region, 5000 to 1333 cm^{-1} (2 to 7.5μ), and the "finger-print" region, 1333 to 667 cm^{-1} (7.5 to 15μ). This is convenient and useful because it is in the higher frequency region that the majority of characteristic functional group absorptions are observed. This is not to imply that none are found in the lower frequency region. A few are. Similarly, the

1333 to 667 cm^{-1} region contains normally the most unique absorptions specific to any given substance.

The interpreter concentrates first on the 5000 to 1333 cm^{-1} region. The strongest bands in this region are given first consideration and the worker starts with the very strongest band. He may, for example, find the strongest absorption at 1740 cm^{-1} . This is most likely an ester carbonyl absorption. And his spectra-structure correlation chart (see Chapter 2 or 6) tells him that an acetate, propionate, or butyrate or longer chain ester are the best possibilities. Following along the chart and looking at other spectral regions where esters show characteristic absorption, it will be seen that the C—O str absorption is observed as a strong band in the 1325 to 1080 cm^{-1} range. Assume the spectrum shows an intense absorption at 1170 cm^{-1} . This is not to be assigned to acetate, most often seen about 1240 cm^{-1} , nor to propionate, usually observed about 1190 cm^{-1} , but to butyrate or longer chain ester. Continuing to follow along the chart in the direction of shorter frequency (longer wavelength), the spectroscopist should now inspect the spectral region near 720 cm^{-1} . Assume the spectrum shows a medium intensity band at 725 cm^{-1} and the sample was scanned in the liquid state. The possibility is now excellent that the unknown contains a saturated aliphatic ester containing an open chain of four or more adjacent methylene groups. The interpreter should make a mental or written note to later compare the spectrum of the unknown against known spectra of such esters. Methyl stearate could be the first choice for comparison purposes, depending on the intensity, number, and form of the absorptions observed between 1390 and 1350 cm^{-1} , which may indicate the type of CH_2 -C grouping(s) present.

The second strongest band in the high frequency region is then considered and assigned to a functional chemical grouping, if possible. Assume this is a 1667 cm^{-1} absorption. An amide carbonyl is a possibility for such a band. The interpreter then proceeds to learn whether this potential amide is unsubstituted (primary), monosubstituted (secondary), or disubstituted (tertiary) by observing the presence or absence of appropriate intensity absorptions in the 1600 and 1150 cm^{-1} , and 1540 cm^{-1} regions.

All the strong bands are studied in the manner indicated above, in order of decreasing intensity until each has been thus examined. Initially the 3.5 μ region of C—H absorption can be disregarded. An organic substance will seldom yield more than four strong absorptions in the 5000 to 1333 cm^{-1} region. More will show three such than any other number of bands. Some, of course, will show only two or even one. When the unknown is a mixture of components, the number of strong bands may well be more than four.

The interpreter then proceeds to the medium intensity absorptions observed in the high frequency region and assigns these with respect to the

functional chemical groupings giving rise to them, to the extent possible. Weak absorption bands in general are not considered at this time. Deciding whether interpretation of weak absorptions will be helpful or necessary is a difficult decision for the beginner. In general, he will normally not try to interpret weak absorption bands, rather using these only in the final confirmation process when he gets to the point of comparing known spectra with the spectrum of his unknown and finds one which matches exactly. To arrive at this confirmation, of course, he will need to consider every absorption band observed, including weak ones.

In the assignment of absorptions in the 5000 to 1333 cm^{-1} region (as also in the 1333 to 667 cm^{-1} region), more than one chemical grouping may be a possibility for a given observed band. Assume an intense absorption is observed at 1695 cm^{-1} . Examination of a correlation chart will show this could arise from the carbonyl of a carboxylic acid, aliphatic or aromatic aldehyde, aliphatic or aromatic ketone, or occasionally even of an amide. The interpreter distinguishes among the above possibilities by observing the presence or absence of absorptions at those other characteristic frequencies where acid, aldehyde, etc., absorb, as tabulated on the assignment chart. Sometimes this procedure by itself will only bring him down to two potentially present functional groups between which he is unable to make a choice. Such a dilemma can only be resolved by comparing a few known spectra of each class of compound against the spectrum of his unknown.

The determination of the presence and type, or the absence of C-H vibrations should be the next point of focus of the interpreter. Alternatively, these absorptions may be considered before any strong bands are examined.

C-H str frequencies occur between about 3200 and 2800 cm^{-1} (in the 3.5μ region). If the band is above 3000 cm^{-1} , then the C atom is unsaturated, or a highly halogenated compound is present. By an unsaturated C atom is meant hydrogen attached to a C atom of the olefinic, aromatic, or acetylenic variety. Chloroform is an example of a highly halogenated substance and its C-H str frequency is observed above 3000 cm^{-1} .

If the C-H absorption is observed below 3000 cm^{-1} , then normally the C atom is saturated, i.e., a tetrahedral C atom is concerned, with all four valences used in bonding to four other atoms. If C-H absorptions are observed both above and below 3000 cm^{-1} , then there are both unsaturated and saturated C atoms present.

Should C-H str frequencies be observed, then the presence or absence of a band about 1460 cm^{-1} should be investigated. If such a band is present, normally less intense than the C-H str frequency, it indicates the probable presence of methyl and/or methylene groupings.

In favorable situations much can be learned about the nature of the C-H present from the presence or absence of a band about 1375 cm^{-1} . A band

near this frequency usually indicates $C-H$. By using his spectra-structure assignment chart, the spectroscopist can often determine something about the type of alkyl group attached to a C atom. Such is often possible for the ethyl, *n*-propyl, isopropyl, or *t*-butyl groupings. For example, if two absorption bands closely spaced on either frequency side of 1375 cm^{-1} are observed and are of about equal intensity, a distinct possibility exists that the isopropyl grouping is present. If a similar situation obtains, but the lower frequency member of the doublet is stronger than the higher frequency one, there is a good possibility of the presence of a *t*-butyl grouping.

A saturated >C-H which contains only one H attached to the C atom yields only a weak absorption near 1350 cm^{-1} and normally no significant absorption between 1370 and 1400 cm^{-1} . Characteristically, polyoxyethylene derivatives, e.g., usually show a weak to medium band near 1350 cm^{-1} , so it is necessary to use caution in assigning the type of saturated >C-H just discussed.

Next in tracking down $C-H$ information, the presence or absence of a medium strength absorption at about 725 cm^{-1} should be investigated. The presence of a single band or a doublet near this frequency normally indicates an open chain of four or more adjacent methylene groupings. A few groupings extremely similar, but not quite identical to a chain of four or more methylenes, also will give an absorption here. In the vast preponderance of instances an open chain of four or more adjacent methylenes is indicated. This absorption will be a singlet, if the spectrum is run in the liquid state, but a doublet when the substance is scanned in the solid state. The investigator should be aware that alicyclic derivatives, such as cyclopentane, cyclohexane, etc., do not yield any absorption here and none will be observed until the saturated alicyclic ring has reached considerable size.

The next procedural step, still considering the high frequency 5000 to 1333 cm^{-1} region, is to determine if possible the general class of organic compound(s) present. The presence or absence, for example, of medium strength 1500 and 1600 cm^{-1} bands indicates the presence or absence of aromatics. The 1600 cm^{-1} region absorption is usually the more useful of the two since it is less often interfered with by nearby absorptions.

The presence of a medium intensity absorption in the 1650 to 1610 cm^{-1} region often indicates the presence of olefins. It should be remembered that in the absence of an absorption in this region an olefin may still be present. When a $C=C$ is located in the center of a symmetrical structure, it normally shows no absorption in this region.

The presence of a weak band about 2210 cm^{-1} , or medium ones at about 3250 cm^{-1} and 2115 cm^{-1} can indicate the presence of an acetylenic deriva-

tive. In the absence of absorption here, acetylenics may still be present for the same reason given above for olefins.

If methylene absorptions are found to be present but no CH_3 -C absorption, the possibility of an alicyclic substance should be looked into.

When the observer identifies the presence of CH_2 and CH_3 groupings and yet no aromatics, olefinics, or acetylenics, the presence of aliphatic compounds should be suspected.

After determining the class of organic compound, then follow through with the spectra-structure assignment chart to define further the acetylenic or olefin, determine the number and position of aromatic substituents present, etc. For example, "aromatic substitution" absorptions are found in the region from about 1225 to 675 cm^{-1} , with those in the region from 900 to 675 cm^{-1} being the most useful. A monosubstituted benzene derivative is characterized by having two strong absorptions at about 700 and 740 cm^{-1} . An *ortho*-disubstituted benzene derivative is characterized by a strong absorption about 750 cm^{-1} and either no absorption or a weak one around 700 cm^{-1} . A *meta*-disubstituted benzene derivative shows strong absorption about 700 and about 775 cm^{-1} . *Para*-disubstitution yields a strong band near 820 cm^{-1} . Similar correlations are available for vicinally, unsymmetrically, and symmetrically trisubstituted benzene derivatives. Correlations have also been found for a few types of substituted naphthalene derivatives.

Should the observer note that only from 3 to 10 mostly broad absorption bands are present in the entire 5000 to 667 cm^{-1} region, and if potential assignments to organic chemical functional groupings lead nowhere, consideration should be given to the possibility that inorganic materials are present. Then the spectroscopist should turn to one of the available spectra-structure assignment charts for inorganics, such as that of Miller and Wilkins.

After the strong absorption bands in the high frequency region have been interpreted, then attention should be focused on the medium intensity bands. When a band does line up for a functional group(s), follow along the assignment chart to determine whether all the absorptions of the group are present. Try to classify the functional grouping as closely as possible: e.g., determine the class of ester, the type of amide, the type of amine, etc. For instance, an ester carbonyl absorption between 1750 and 1730 cm^{-1} is likely to arise from a saturated ester, while an ester carbonyl absorption observed between 1730 and 1715 cm^{-1} is likely to arise from an unsaturated ester.

Once a spectroscopist has garnered the maximum amount of useful information from the high frequency region, he should concentrate on the 1333 to 667 cm^{-1} region, proceeding as before, from the strong bands to medium intensity ones.

When the interpretation of the spectrum reaches the stage of suggesting a certain specific compound(s) may be present, comparison should then be made with the spectra of such knowns for a final identification. It is well to remember that the identification of an unknown is not complete or certain until a known spectrum can be found which matches that of the unknown in every detail.

If comparison against known spectra shows that more than a single component is present in the unknown, the absorption bands belonging to the first component identified should be marked off, and the spectroscopist can then proceed to interpret the remaining bands in a manner already indicated above. When the entire spectrum of an unknown has been matched by the sum of several known spectra, no further infrared-absorbing chemical components are present in the unknown in significant percentage.

HELPFUL RULES OF THUMB

During the course of interpretation of a spectrum it is helpful to bear in mind certain general considerations. The absence of an absorption band is more convincing evidence of a functional group's absence than the presence of a band is evidence of its presence. This is true because absorptions in most regions of the spectrum can arise from more than one functional grouping or other structural feature.

All the bands observed in a spectrum can never be interpreted — some are absorptions of the molecule as a whole, some are combination bands, and some are overtone bands. A given absorption may arise from the coupling of several vibrations and thus not be assignable to any specific functional grouping or specific structural feature.

Eight to ten components are about the most which can be identified in the spectrum of a mixture. Occasionally fewer are identifiable. The similarity and the structural complexity of the components present will determine how large this number can be. The more widely different the components are from each other in chemical structure and element composition, the larger the number of components which can be identified in a mixture.

It should be remembered that absorptions at about 3350 and 1645 cm^{-1} often indicate the presence of water in a sample. It is easy to forget this if, during the sample preparation, the material appears to be "dry."

Polymers in general have fewer, broader, and often less intense bands than the monomers from which they are derived.

Try as he will, the spectroscopist will be unable to identify some unknowns. Certain of these unidentifiable materials may be identified at a future date as new spectra-structure correlations are learned and spectra of new knowns run. The identity of others may perhaps elude the investigator indefinitely. It is well to keep in mind that many molecules of complex

structure cannot be identified from their infrared spectra alone. The resourceful infrared spectroscopist will realize when he is licked, and turn to other complementary techniques. The power of x-ray spectroscopy, emission spectroscopy, NMR, mass spectroscopy, and ultraviolet spectroscopy should not be overlooked in the judicious selection of complementary techniques. If one is willing to pay the price in effort, there is probably no single organic substance now extant or to be synthesized or isolated in the future whose chemical structure can not be determined.

INTERPRETATION OF SPECTRA — EXAMPLES

Experience is the best teacher of spectral interpretation. The beginner will find it helpful to scan the spectra of a few simple substances representing different classes of compounds and then interpret them on the basis of their known chemical structures using an appropriate spectra-structure correlation chart. He could select methane, ethylene, acetylene, benzene, carbon disulfide, carbon tetrachloride, methyl acetate, *n*-amyl ether, acetaldehyde, methyl ethyl ketone, propionic acid, *n*-butyl amine, propionamide, and benzene sulfonic acid to give him some experience with organic chemicals. What the novice chooses for learning purposes should be governed by the type of problems with which he expects to be confronted. The spectroscopist in the polymer field, e.g., will want to become familiar with the spectra of monomers, polymers, copolymers, stabilizers, antioxidants, and the like.

Unknown Plasticizer

Figure 5-1 presents the 4000 to 667 cm^{-1} (2.5 to 15 μ) spectrum of a liquid material scanned at capillary thickness between NaCl plates in air using a prism spectrophotometer. This nearly water-white liquid was extracted from

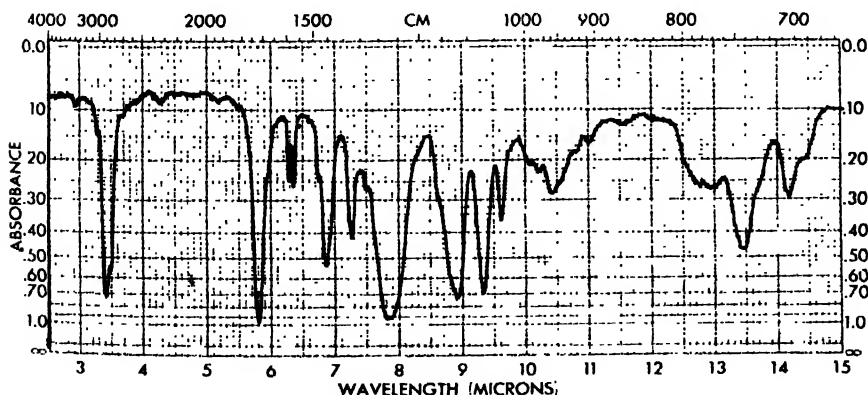


FIGURE 5-1. Infrared spectrum of polymer extract.

a flexible polymer formulation and is suspected to contain one or more plasticizers.

The strongest band observed in the 4000 to 1333 cm^{-1} region is the one at 1724 cm^{-1} (5.80μ). Study of the possibilities for such an absorption, using an assignment chart, indicates an ester carbonyl is most likely. This 1724 cm^{-1} band is seen to be the only strong band in the high frequency region except for the 2933, 2857 cm^{-1} ($3.41, 3.50\mu$) doublet and the 1458 cm^{-1} (6.86μ) absorption. The doublet absorption indicates C—H str probably of CH_2 and/or CH_3 . The 1458 cm^{-1} band indicates C—H bending probably of CH_2 and/or CH_3 . Since a 1376 cm^{-1} (7.27μ) absorption is present, CH_3-C suggests itself as a possibility. No suggestion of isopropyl or *t*-butyl groupings is observed. The very weak absorption at 1333 cm^{-1} (7.50μ) suggests

the possible presence of the $\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array}$ H grouping—only one H attached to this saturated carbon. Looking in the 725 cm^{-1} (13.8μ) region, an indication of a band is seen at about 730 cm^{-1} (13.70μ). Since it is enveloped by a much stronger nearby absorption, one can't be sure whether or not an open chain of four or more adjacent methylene groups is present. The possible presence of this structural feature or one structurally close to it should be considered a possibility.

Returning to the ester carbonyl, attention is now focussed on the regions of ester C=O absorption. A strong band at 1274 cm^{-1} (7.85μ) informs, after study of the various possibilities, that a benzoate or phthalate ester is most likely, since a strong absorption is also observed at 1122 cm^{-1} (8.91μ).

From the rather large number of absorption bands observed in the Figure 5-1 spectrum, an organic material is obviously present. What general class of organic substance is it? A doublet is seen at 1592 cm^{-1} (6.28μ) and 1575 cm^{-1} (6.35μ). Together with the 1481 cm^{-1} (6.75μ) band, this means an aromatic derivative is present. After minimal experience with ester spectra, the spectroscopist will quickly realize the 1592, 1575 cm^{-1} doublet most often indicates the presence of an *o*-phthalate ester. Inspection of the spectrum for olefinics and acetylenics reveals no indications of the presence of these classes of organics.

At this point in the interpretation, the spectroscopist could compare the spectrum of the unknown liquid with known spectra of *o*-phthalate esters and would soon find a spectral match and identification of the unknown, provided the spectrum of the specific ester present was in his spectra file. Further consideration can be given to the spectrum, however, to make spectral comparisons against knowns less tedious.

The relative intensities of the C—H absorptions at 2933, 2857, 1458, and 1376 cm^{-1} compared, e.g., to those of the ester carbonyl and ester C—O

bands suggest the presence of a relatively large number of methylene groupings and very probably more than one $\text{CH}_2 - \text{C}$ grouping. The possibility of the presence of a 730 cm^{-1} band indicates an open chain of four or more adjacent methylenes or very similar structural moiety is possibly present. The 1333 cm^{-1} band gives additional indication that a branched alkyl chain may be present.

Since the unknown liquid was extracted from a commercial polymer formulation, the interpreter knows he is dealing with an item of commerce, not a new substance. Knowing the plastic from which the extraction was made and aware of the information already uncovered by spectral interpretation, the spectroscopist would probably begin his comparisons against known *o*-phthalate esters with di(2-ethylhexyl) phthalate, the popular DOP. He would find all the significant bands observed in the spectrum accounted for by DOP. The unknown liquid is then di(2-ethylhexyl) phthalate only, with traces of impurities.

The reader will note that no attention was paid to bands in the fingerprint region, 1333 to 667 cm^{-1} , with the exception of the 1274 , 1122 , and 730 cm^{-1} absorptions. It was not necessary. For practice the spectroscopist can locate the *o*-disubstituted benzene absorptions and those characteristic of the ethyl grouping.

Experience in differentiating among various *o*-phthalate esters, many of which are used as plasticizers, will soon teach the investigator that the 900 to 1000 cm^{-1} region is an excellent one to use to distinguish among them. Practically all such esters have uniquely characteristic absorptions in this region.

It should be noted that the spectrum of Figure 5-1 was scanned on a tabletop spectrophotometer. The frequencies of observed absorptions will not be precisely the same when this liquid is scanned on a more sophisticated prism instrument or on a grating spectrophotometer.

Unknown Solvent

A chemist finds the crayon marking identifying a 10 liter flask of solvent, used in a project temporarily set aside for several months, is no longer legible. He believes from the odor and his recollection that he knows what the solvent is, but is not sure. Scanning the spectrum of this liquid at a capillary thickness between NaCl plates vs air on a tabletop spectrophotometer yields Figure 5-2.

The strongest band in the 4000 to 1333 cm^{-1} range is observed at 1701 cm^{-1} (5.88μ). Study of the assignment chart indicates a carbonyl grouping of an acid, aldehyde, or ketone. An acid is out because of the lack of a strong absorption near 1260 cm^{-1} ; the chemist definitely remembers he wasn't using any acid. Nor is the solvent's odor acid-like. No medium intensity

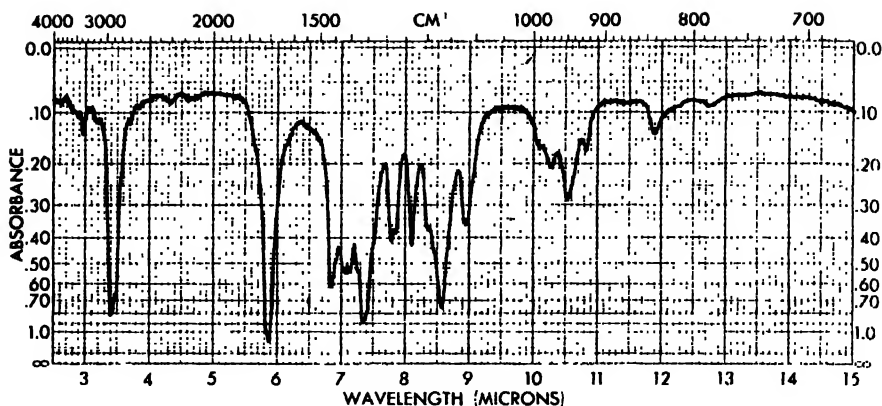


FIGURE 5-2. Infrared spectrum of unknown solvent.

band is observed close to 900 cm^{-1} , which rules out an aldehyde. The presence of a 1166 cm^{-1} (8.58μ) absorption at medium-plus intensity indicates an aliphatic ketone is a good possibility. Lack of any bands near 1600 and 1500 cm^{-1} shows no aromatics. The likely ketone carbonyl absorption (1701 cm^{-1}) is the only strong non C—H absorption in the high frequency range.

Turning to the class of organic present, no evidence is seen for other than an aliphatic compound.

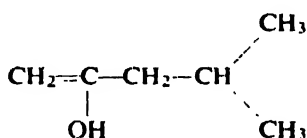
The C—H str bands at 2941 (3.40μ) and 2865 (3.49μ) suggest CH_3 and/or CH_2 . The C—H bending absorption at 1460 cm^{-1} (6.85μ) suggests the same groupings. In the C—H bending region which yields information on the type of CH_3 —C linkage present, a medium intensity doublet is observed at 1414 cm^{-1} (7.07μ) and 1403 cm^{-1} (7.13μ). Notably these two bands are about equal in intensity and indicate the possible presence of the isopropyl grouping. The weak absorption comprising the isopropyl triplet in this region arising from the >C—H and occurring between 1350 and 1310 cm^{-1}

is rather “washed out” by the strong band at 1362 cm^{-1} (7.34μ). This absorption makes known that a CH_3 —C grouping, in addition to a possible isopropyl, is also probably present. Pursuing the isopropyl possibility further, a medium intensity band at 1116 cm^{-1} (8.96μ) is present and a medium intensity band about 1160 cm^{-1} would be obscured by the strong ketone C=O absorption at 1166 cm^{-1} . Or the high frequency shoulder on this band may represent the other member of the medium intensity duo normally found between 1200 and 1100 cm^{-1} . Getting back to further C—H information available from the spectrum, no indication is seen near 725 cm^{-1} for the presence of an open long methylene chain.

The strong and medium intensity bands in the high frequency range have been dealt with. Attention now turns to the 1333 to 667 cm^{-1} fingerprint region. The only strong band, 1166 cm^{-1} , has been assigned. Two medium intensity absorptions have been assigned. The temptation to spend time interpreting other medium strength bands in the 1333 to 667 cm^{-1} range should be resisted. Experience correlating many spectra intuitively suggests that a band near 950 cm^{-1} rather often points to the presence of the butyl grouping. Neglecting this last bit of information the assemblage of spectrally interpreted information is now appropriate. The unlabeled solvent is an aliphatic ketone with a $\text{CH}_3\text{—C}$ and an isopropyl grouping. Comparing its spectrum against that of known methyl isopropyl ketone shows a similarity but no spectral match.

At this juncture it is well to recall that the isopropyl grouping is also present in the isobutyl, isoamyl, etc., radicals. Comparison is next made against the known spectrum of methyl isobutyl ketone (MIBK) and this shows the unknown solvent is MIBK only.

The Figure 5-2 spectrum of MIBK, analytical reagent grade having 0.001% residue after evaporation and 0.01% acidity, shows the presence of a 3365 cm^{-1} (2.97μ) nonwater hydroxyl absorption. This is believed to be the O—H str of the tertiary alcohol grouping arising from the presence in MIBK of a very small percentage of the structure



Unknown Pharmaceutical Component

Figure 5-3 represents the 4000 to 667 cm^{-1} spectrum of a colorless liquid scanned between NaCl plates at capillary thickness vs air on a tabletop prism spectrophotometer. Since this somewhat viscous liquid was extracted from a pharmaceutical formulation taken internally, the identity of a nontoxic material is sought.

The only strong band in the characteristic functional group region 4000 to 1333 cm^{-1} is that at 3333 cm^{-1} (3.0μ). Since no evidence is seen for the presence of significant water absorptions between 2500 and 2000 cm^{-1} (4 to 5μ) nor at 1645 cm^{-1} (6.08μ), this 3333 cm^{-1} absorption probably arises from a bonded hydroxyl. A hydrogen-bonded N—H str band at this frequency would be narrower in band width. The possibility of the presence of an N—H absorption here, however, cannot be ruled out on the basis of this band alone. It could be present and obscured by the broader O—H. No evidence is observed for amines near 1600 cm^{-1} (6.25μ) or 1550 cm^{-1}

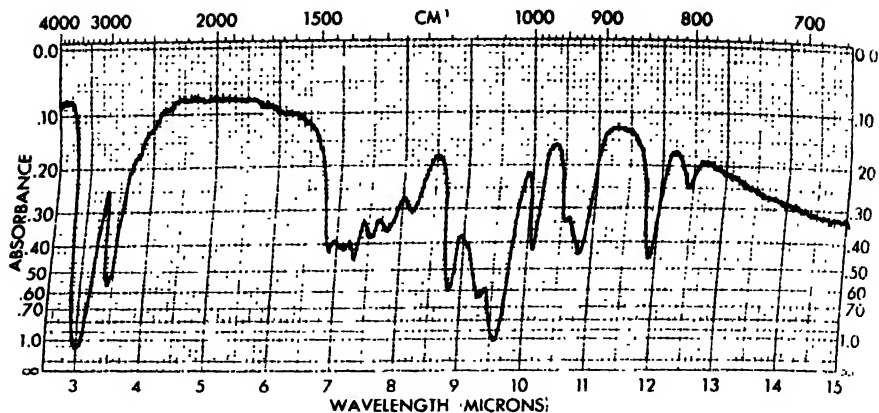


FIGURE 5-3. Infrared spectrum of pharmaceutical component.

(6.45 μ), for amides near 1667 cm^{-1} (6.00 μ) or 1600 cm^{-1} (6.25 μ), nor for imines near 1660 cm^{-1} (6.02 μ). It is then safe to conclude the 3333 cm^{-1} band arises only from an alcoholic hydroxyl, since no carbonyl absorptions of any type are seen in the 1875 to 1550 cm^{-1} range. Pursuing the class of alcohol concerned, the strong band at 1044 cm^{-1} (9.58 μ) suggests the presence of primary alcohol. The absorptions at 1136 (8.80 μ), 1285 (7.78 μ), and 1406 cm^{-1} (7.11 μ) indicate the likely presence of a secondary alcohol as well. The temptation may be present to assign the 1136 cm^{-1} band to an aliphatic ether since this grouping shows absorption in this region. An aliphatic ether band is usually a strong one, and the 1136 cm^{-1} absorption is medium intensity. No band is observed near 1175 cm^{-1} , so a tertiary alcohol is not likely. Aromatic alcohol can be ruled out because no aromatic absorptions are seen at either 1600 or 1500 cm^{-1} . The conclusion to this point is that an alcohol is present which is both primary and secondary, or that two alcohols are present — a primary and a secondary. Other possible combinations of these two functional groupings come readily to mind.

Focussing again on the 4000 to 1333 cm^{-1} region, consideration is given to C—H absorptions. The triplet whose strongest member occurs at 2933 cm^{-1} (3.41 μ) suggests the presence of CH_3 and/or CH_2 ; the 1451 cm^{-1} (6.89 μ) band also indicates CH_3 and/or CH_2 ; the 1374 cm^{-1} (7.28 μ) absorption suggests $\text{CH}_3\text{—C}$; and the 1328 cm^{-1} (7.53 μ) band brings to mind the possible presence of >C—H . No evidence is observed near 725 cm^{-1} for an open chain of four or more adjacent methylenes.

Considering the class of organic compound(s) present, no spectral evidence is apparent for other than aliphatics.

Having disposed of the high frequency region, attention is turned to the 1333 to 667 cm^{-1} range. Four absorptions therein have already been assigned. The spectroscopist may now attempt to interpret, e.g., the 840 (11.90μ), 926 (10.80μ), 990 (10.09μ), and 805 cm^{-1} (12.42μ) bands. He will find no assignments helpful to the identification of this unknown. In fact, if he persists in trying to assign the bands mentioned above he will perhaps confuse the situation by finding indications for the presence of epoxy ring, e.g., and other structural features which are not present. How does he know when to quit interpreting absorptions? Since he already has considerable information about the unknown at hand, now is the time to decide to make comparisons against known spectra. As a general rule, when identification is the objective, under-interpretation is more fruitful than over-interpretation.

In considering which known spectrum to compare against first, one naturally chooses that of the simplest molecule conceivable which is compatible with the interpretive findings. What molecule contains both a primary and secondary alcohol grouping, a CH_3 C grouping, and a $\text{C}-\text{H}$? Propylene glycol fits these findings. Spectral comparison shows the extracted pharmaceutical component is propylene glycol only. And it is a colorless, somewhat viscous liquid that can be safely taken internally.

Elastomer Component

The solvent-insolubles from a rubber formulation were separated as a white powder. A pigment and/or filler was suspected and its identity sought. Figure 5-4 shows the 4000 to 667 cm^{-1} spectrum of this powder scanned as a Nujol mull vs air. Nujol absorptions are observed, as usual, at 2933 (3.41μ),

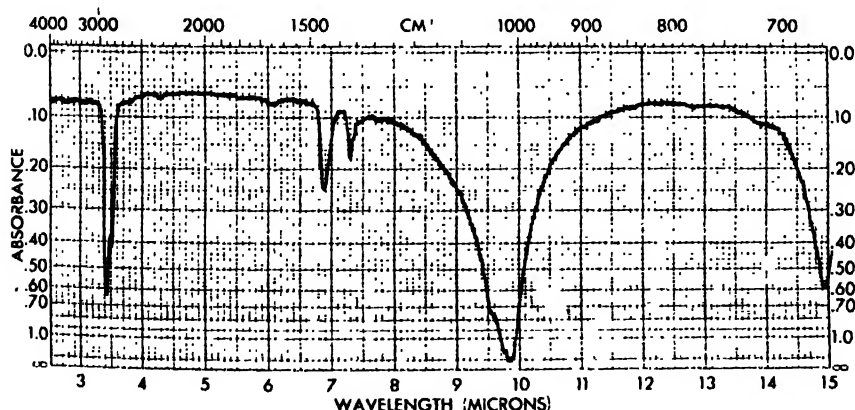


FIGURE 5-4. Infrared spectrum of elastomer component.

2849 (3.51μ), 1451 (6.89μ), 1370 (7.30μ), and 720 cm^{-1} (13.9μ) and are to be disregarded. The hexachlorobutadiene mull of the unknown powder (not shown) showed no absorptions in the 2.5 to 4, 6.5 to 7.8, and 13.5 to 14.3μ regions.

The few absorption bands given by this sample, the lack of any characteristic functional group absorptions in the 4000 to 1333 cm^{-1} region, the absence of any C—H bands, and its solvent-insoluble nature all point to an inorganic. Turning to an assignment chart for inorganics, such as the well known one by Miller and Wilkins, the very strong 1015 cm^{-1} (9.85μ) band is seen to arise most likely from a silicate, tribasic phosphate, or dibasic phosphate. Spectral comparison against known spectra of such materials quickly shows the unknown powder is talc, hydrous magnesium silicate, only.

Paper Coating Component

The solvent-solubles from a paper coating were found to be film-forming. Films were cast from hot methyl ethyl ketone (MEK) solution onto NaCl plates at progressively increasing solute concentration. Residual MEK was evaporated off in an oven at 95°C for two hours. Figure 5-5 presents the 4000 to 667 cm^{-1} spectrum of the paper coating component scanned as an evaporated film vs air. Two scans, at different film thicknesses, are shown.

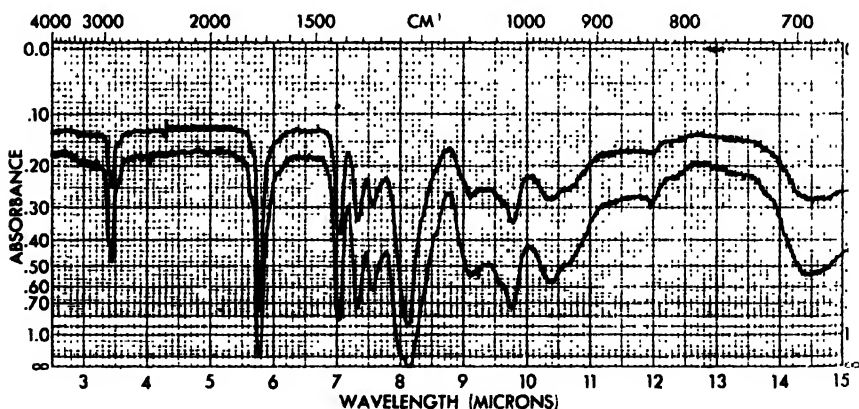


FIGURE 5-5. Infrared spectrum of paper coating component.

The “pips” at 4.04 , 4.30 , 9.24 , and 11.95μ arise from unwanted “noise” and are to be disregarded. At times the best of spectrophotometers misbehave, sometimes explicable, sometimes inexplicable. The presence of a polymeric component(s) is suspected based on the end-use of the coated paper and the film-forming ability of the MEK extract. In the 4000 to

1333 cm^{-1} region the strongest band is that at 1730 cm^{-1} (5.78μ). The assignment chart informs this absorption probably arises from an ester carbonyl.

Before proceeding further, the investigator should be aware that polymeric materials in general are not easily freed of small percentages of residual solvent. The first step here, as with the spectra of all polymers scanned as evaporated films cast from solution, is the comparison of the spectrum against that of the solvent used, MEK in this case. The shoulder absorptions at about 1709 cm^{-1} (5.85μ) and 1170 cm^{-1} (8.55μ) arise from the presence of residual MEK. No other spectral evidence for MEK is observed.

Turning to the type of ester present, the 1233 cm^{-1} (8.11μ) band suggests only acetate since no other strong absorption is seen at about 1160 cm^{-1} which would have made a maleate ester a possibility.

The type of C-H present is now considered because the 1730 cm^{-1} band is the only strong one between 4000 and 1333 cm^{-1} . The 2915 cm^{-1} (3.43μ) absorption together with that at 2857 cm^{-1} (3.50μ) suggests CH_3 and/or CH_2 . The shoulder at 2950 cm^{-1} (3.39μ) is observed to be quite different from any seen in the spectra of materials given earlier in this chapter. Study of the possibilities suggests perhaps a methyl or methylene group adjacent to a carbonyl, or possible unsaturated carbons. Since no significant absorptions are observed for acetylenics, olefinics, or aromatics, the possibility for unsaturation is less but cannot be discarded. Significantly no 1460 cm^{-1} absorption is observed. The ordinary type of CH_3 and/or CH_2 bending is thereby not present. A band is seen at 1368 cm^{-1} (7.31μ) from the probable presence of CH_3-C . The absorption at about 1325 cm^{-1} (7.55μ) suggests the likely presence of considerable >C-H . No evidence for an open chain of four or more adjacent methylenes is observed near 725 cm^{-1} .

Considering now the medium strength bands in the 4000 to 1333 cm^{-1} region, the 1425 cm^{-1} (7.02μ) absorption is the only one not already assigned. Study of the possibilities indicates a methyl adjacent to a carbonyl is more likely, based on intensity, than a methylene adjacent to a carbonyl.

Turning to the 1333 to 667 cm^{-1} fingerprint region, the strongest band not yet considered is the medium intensity absorption at 1025 cm^{-1} (9.76μ). While various possibilities could be assigned to this band, probably none of them would aid the identification. In fact, they could easily confuse. Since every indication says the extract is polymeric and an acetate ester is a likely presence, comparison should now be made against the known spectra of polymeric acetates. Polyvinylacetate (PVAc) immediately comes to mind. Long before this point had been reached, the spectroscopist with minimal experience in polymers would have recognized the 1099 cm^{-1}

(9.10 μ) and 1025 cm^{-1} bands together with the acetate ester information as indicating the presence of a PVAc copolymer. And the presence of the characteristic broad absorption centering at about 689 cm^{-1} (14.50 μ) would tell him a VC (vinyl chloride)-VAc copolymer was present. The investigator, unfamiliar with this latter knowledge, could come to the conclusion that an aliphatic C—Cl grouping was probably present, from interpretation of the 689 cm^{-1} band using his assignment chart.

Comparison against known spectra would show that the paper coating component is comprised of VC-VAc copolymer. The uncaredful spectroscopist might now feel elated at his "successful" identification. He could perhaps be excused for his incomplete result should he be lacking known spectra of various types of modified VC-VAc copolymers. Careful observation, however, should arouse his curiosity about the shoulder absorption at 1779 cm^{-1} (5.62 μ). Straight VC-VAc copolymers show no absorption here. Study of the assignment chart would show the likely presence of a carbonyl grouping. This leads one to suspect modification of the copolymer by an acid, anhydride, etc. Actually the paper coating spectrum is that of VC-VAc copolymer, maleic anhydride modified, or a VC-VAc maleic acid terpolymer, as one prefers to name it. Very probably the precise identification of the modifying component can not be made by infrared alone, unless one has a spectrum of the known material available.

The illustrations of qualitative interpretation of infrared spectra given above are intended only as a bare beginning for the budding spectroscopist. He should scan or dig out from appropriate catalogs the spectra of a wide variety of organic and inorganic chemicals and interpret them to the extent possible in terms of characteristic functional groups and other structural features. He can progress from simpler molecules to more complex ones and then try mixtures, gradually increasing the number of components present. It will profit any spectroscopist to study the spectra of series of homologous and analogous compounds in order to improve his interpretive capabilities. Such a course will bring proficiency much more quickly than waiting to acquire spectra-structure knowledge through experience as problems develop in, or are submitted to, his laboratory.

For reference, an outline of the general procedure for qualitative interpretation of spectra presented in this chapter is given below.

OUTLINE OF A GENERAL PROCEDURE FOR QUALITATIVE INTERPRETATION OF INFRARED SPECTRA

I. Value of Sample History

- (A) Bear in mind throughout the interpretation and apply all available information about the unknown such as:

- (1) Chemical elements known to be present
- (2) Chemical elements known to be absent
- (3) Physical state and color
- (4) Purity of unknown whether a single compound or mixture
- (5) Use which is made of unknown
- (6) Possible component(s) present

II. Spectral Interpretation Procedure

(A) Divide rocksalt Infrared into characteristic functional group region, 5000 to 1333 cm^{-1} (2 to 7.5μ), and the fingerprint region, 1333 to 667 cm^{-1} (7.5 to 15μ).

- (1) Concentrate first on 5000 to 1333 cm^{-1} region; consider strongest absorptions, then medium ones (weak ones only if necessary and helpful).
- (2) Determine presence and type, or absence, of C—H vibrations.
 - a. C—H frequencies occur between 3200 and 2800 cm^{-1} .
 - b. If above 3000 cm^{-1} , then C atom is unsaturated or a highly halogenated compound is present.
 - c. If below 3000 cm^{-1} , then C atom is saturated.
 - d. If both above and below 3000 cm^{-1} , then C's are unsaturated and saturated.
 - e. Band about 1455 cm^{-1} indicates CH_3 and/or CH_2 .
 - f. Band about 1375 cm^{-1} indicates $\text{C}\equiv\text{CH}_3$.
 - (1) Use assignment chart to determine whether ethyl, *n*-propyl, isopropyl, or *t*-butyl.
 - g. Medium band about 725 cm^{-1} indicates open chain of 4 or more adjacent methylenes.
- (3) Determine, if possible, the class of compound(s) present.
 - a. Presence or absence of medium strength 1500 and 1600 cm^{-1} bands indicates presence or absence of aromatics.
 - b. Presence of medium 1650 to 1610 cm^{-1} band indicates presence of olefin (in absence olefin may still be present).
 - c. Presence of weak band about 2210 cm^{-1} or a medium one at 3250 cm^{-1} and a medium one at 2115 cm^{-1} indicates presence of an acetylenic derivative (in absence acetylenic may still be present).
 - d. If CH_2 present but no $\text{CH}_3\text{—C}$ investigate possibility of alicyclics.
 - e. If CH_2 and CH_3 present and no aromatic, olefinic, or acetylenics, suspect presence of aliphatic compound(s).
 - f. After determining compound type, follow through to learn type of olefin, number and position of aromatic substituents, etc.

- g. If only from 3 to 10 bands present with several broad ones, or if organic assignments of bands lead nowhere, consider possibility of inorganics — use Miller and Wilkins assignment chart, e.g.
 - (4) Proceed to interpret strong bands, then medium ones. If a band lines up for a functional group(s), follow along to determine whether all absorptions of the group are present, and to classify it as closely as possible, e.g., class of ester, type of amide, class of amine, etc.
 - (B) Concentrate next on 1333 to 667 cm^{-1} region, proceeding from strong bands to medium ones as in II, A, 4.
 - (C) When interpretation reaches stage of suggesting presence of possible compound(s), comparison should be made with the spectra of knowns for final identification.
 - (1) If this comparison shows more than a single component is present, mark off absorptions belonging to the first component identified, then proceed to interpret remaining bands as above.
- III. Helpful Rules of Thumb**
- (A) Absence of absorption band is more convincing evidence of a functional group's absence, than presence of a band is evidence of its presence.
 - (B) All the bands in a spectrum can never be interpreted — some are absorptions characteristic of the molecule as a whole, some are combination bands, and some are overtone bands. ~
 - (C) Eight to ten components are about the most that can be identified in a mixture (sometimes fewer, depending on the similarity and structural complexity of the components).
 - (D) Presence of bands about 3350 and 1645 cm^{-1} often indicates presence of water in a sample.
 - (E) Polymers in general have fewer, broader, and often less intense bands than the monomers from which they are derived.
 - (F) Some unknowns one will not be able to identify. Of these, some may be identified later as new correlations are learned and spectra of new knowns run --- the identity of others may perhaps elude one indefinitely. For these, use complementary techniques - NMR: x ray, Mass, UV, Emission Spectroscopy; VPC, etc.

CHAPTER

6

Infrared on the Chemist's Bench

*R. D. Moss, W. J. Potts, Jr.**

INTRODUCTION

Advantages for the Chemist

Many chemists think of infrared only as a tool for the theoretical man concerned with structural analysis or for the analyst concerned with semi-routine analyses. However, the specificity of infrared leads to truly enormous benefits to the chemist who will use it on his bench to follow syntheses and process studies.

To quote Professor R. B. Woodward¹⁸ "... No single tool has had a more dramatic impact upon organic chemistry than infrared measurements. The development, just after the second Great War, of sturdy and simply operated machines for the determination of infrared spectra has permitted a degree of immediate and continuous analytical and structural control in synthetic organic work which was literally unimaginable fifteen years ago. The power of the method grows with each day, and further progress may be expected for a long time to come. Nonetheless, its potentialities are even now greater than many realize, and two special pleas may perhaps be permitted. . . . The routine examination of virtually every reaction mixture, however crude, or lacking in tangible prospect of yielding a desired product, often provides a clue to important developments which could not otherwise be made . . . The capacity of the physical specialist to place his results properly in the context of an organic chemical investigation is often narrow and unrealistic, and the organic chemist will find himself magnificently re-

**The Dow Chemical Company, Midland, Michigan*

warded, who takes the pains to be himself in a position to understand and interpret the physical aids he wishes to use. In any event, physical methods and the principle that they should be used whenever possible, are now part of our armamentarium, and we may expect no surcease of further developments in this direction."

With mounting research costs it has become mandatory that chemists adopt methods which will enable them to obtain rapidly the most accurate data to guide their research and development efforts. Infrared, used on the chemist's bench, offers a method for the chemist to check starting materials, follow reactions and guide purifications while work is in progress. Thus the chemist can avoid some of the pitfalls caused by impure reagents, improper reaction conditions and inadequate purification procedures. Based upon infrared evidence, process conditions can be modified in time to save unnecessary experiments. Likewise in kinetic and process studies the infrared examination of samples of a single reaction mixture at appropriate time intervals can provide the information often otherwise obtainable only by a series of experiments.

The infrared method offers a positive approach to analysis. In many cases pure compounds may be identified with certainty by virtue of their infrared "fingerprint." Traditional analytical tools, exemplified by elemental analyses, freezing points, refractive indices and densities, can give a fairly positive identification of pure compounds, but they are of little value for complex mixtures or even for the simplest mixtures of unanticipated composition. On the other hand, the indication of certain structural features by the infrared spectrum can often result in the identification of an unsuspected intermediate or by-product.

Another advantage which many researchers have come to appreciate is that the infrared method can be applied to practically all materials. With relatively simple techniques infrared spectra can be obtained of solids, liquids and gases, regardless of solubility, molecular weight, apparent opacity, or number of components. Thus infrared can be applied to a wide variety of problems which the synthetic chemist may encounter.

The infrared spectrum enables the chemist to obtain a permanent record of the progress of his research. The importance of such a record cannot be overemphasized. During the latter stages of research projects it is amazing how often additional information will make possible the identification of that "perplexing carbonyl component" encountered in earlier experiments. Furthermore, due to its specificity, an infrared spectrum offers the best possible patent evidence.

The use of infrared on the chemist's bench was given a tremendous boost by the first introduction of low-priced instruments in 1957. Such instruments in the \$4000 to \$6500 price range, marketed by several manufacturers,

offer adequate resolution and precision to solve a high proportion of the chemist's infrared problems. These instruments are simple and compact. Anyone can obtain reasonably excellent spectra with relatively little instruction. Furthermore, the manufacturers of these instruments supply such simple instruction and maintenance manuals that it is no longer necessary to be an electronics or optics engineer to maintain a spectrometer at its top operating performance. Thus it is no wonder that the infrared spectrometer is fast becoming standard equipment in industrial as well as academic research and development laboratories, taking its place alongside the analytical balance and the melting point apparatus.

It is the purpose of this chapter to describe some of the techniques which may be employed by the bench chemist to capitalize fully on the advantages to be gained through judicious use of the infrared method.

INSTRUMENTATION AND EXPERIMENTAL TECHNIQUES

Tabletop Spectrometers

Description. The commercial development of low-cost bench-top spectrometers in 1957 has given the organic chemist a laboratory tool with which he can solve rapidly many of his analytical and structural problems. These instruments as supplied by leading manufacturers incorporate the following desirable features:

Double-beam, optical null system. The double-beam system has the advantage that it produces a net transmission spectrum directly, without the necessity of replotting data. Extraneous background interferences such as atmospheric absorption, source fluctuations, amplifier gain change or changes in optical surfaces are automatically cancelled out. Double beam operation permits cancelling weak solvent absorption and allows low concentrations to be measured by differential analysis. In certain cases this technique permits very small differences in two similar samples to be magnified for exact quantitative measurements. The null method eliminates the necessity for preliminary runs or waiting time for successive operations.

Simplicity and speed of operation. A minimum of controls and "gadgets" is required for instrument operation. Spectra are recorded automatically with a minimum scanning time consistent with adequate resolution and accuracy.

Compact, rugged design. The instrument should fit on a lab bench or desk with room to spare and needs no external components such as batteries and voltage regulators. A simple, rugged design makes possible comparatively trouble-free operation even in the hands of relatively inexperienced operators.

The infrared spectrometer type having the widest use today is the NaCl prism spectrometer; it covers, with reasonable resolution, the spectral region from 2.5 to 15 μ , the range in which the majority of chemical applications occur. The advantage of this spectrometer type is its low cost. Very recently, however, grating spectrometers have become available in "bench-top" models, and these spectrometers, while somewhat more expensive, provide certain advantages: certain models of grating spectrometers have extended spectral ranges, some going to wave lengths as low as 0.83 μ , others to wave lengths as long as 25 μ ; a second, more important advantage of grating spectrometers is their increased resolution; compared to NaCl spectrometers they offer approximately a factor of two better resolution at 14 μ on up to as much as a factor of 15 at 2.5 μ . Our experience indicates that this high factor of resolution increase at shorter wave lengths (where it is most important) easily justifies the 30 to 60% increase in cost of the spectrometer.

Setting Up the Tabletop Spectrometer. While these tabletop spectrometers are rugged and are designed for operation under less than ideal conditions, the researcher will be rewarded by better performance if he exercises reasonable care in setting up the spectrometer in the laboratory. It should be placed on a sturdy table in an area free from vibration and where there is little likelihood of chemical spills. Because water is particularly detrimental to sodium chloride cells and optics, a location near water and steam outlets is to be avoided. Air conditioning and humidity control are not absolutely essential, due to temperature-compensating devices as well as desiccated monochromator units in these instruments. There is no doubt, however, that the cleaner atmosphere associated with air-conditioned surroundings will result in less deposit of dust and chemical films on the electronics and optics and thus reduce maintenance. We have found it advisable to have the instrument turned on and maintained on a stand-by basis 24 hours a day so that it will always be available for instant use without any warm-up period. The heat generated by the source and tubes will also aid in maintaining a dry internal atmosphere.

It is necessary to provide a ventilated sample preparation area, preferably a hood, adjacent to the spectrometer to remove toxic carbon tetrachloride and flammable carbon disulfide vapors as well as to facilitate handling odoriferous and toxic samples. A source of dry, filtered air for drying cells as well as a storage cabinet for cells is required in this area. A cell-storage cabinet such as a stainless steel desiccating cabinet* is much preferable to the often used desiccators.

Spectrometer Maintenance and Testing. Best work can be done only when the spectrometer is performing at its maximum capability. Although de-

*Available from Aloe Scientific Apparatus Company.

signed to be as rugged as possible, it must be recognized that infrared spectrometers do need regular checking. Therefore, it is strongly recommended that the following tests be made regularly, preferably daily. Less than 45 min is required for a complete spectrometer performance check.

Wavelength accuracy can easily be checked by obtaining the spectrum of a standard material. A thin film of polystyrene in a convenient cardboard mounting, with precise values of the wavelengths of the absorption bands indicated, is supplied with most spectrometers for this purpose. If the wavelengths of the absorption bands are not observed at their correct values within reasonable tolerance, adjustments must be made. The level of 100% transmission should be checked by obtaining a scan with no materials in either spectrometer beam. Unless a reasonably flat line is obtained, the spectrometer is not operating properly; dirty optical parts are the most common trouble. The level of 0% transmission should be checked by obtaining a scan with a thin piece of glass in the sample beam. Beyond 4μ the transmission level should be a line reasonably colinear with 0% transmission (infinite absorbance). If uniform, but not at 0% transmission, a simple adjustment is required; but if the line is not flat, scattered light is probably present in the spectrometer. Response (gain), and drift should also be checked in accordance with methods described in the instruction manual. Figure 6-1 shows an example of a performance check.

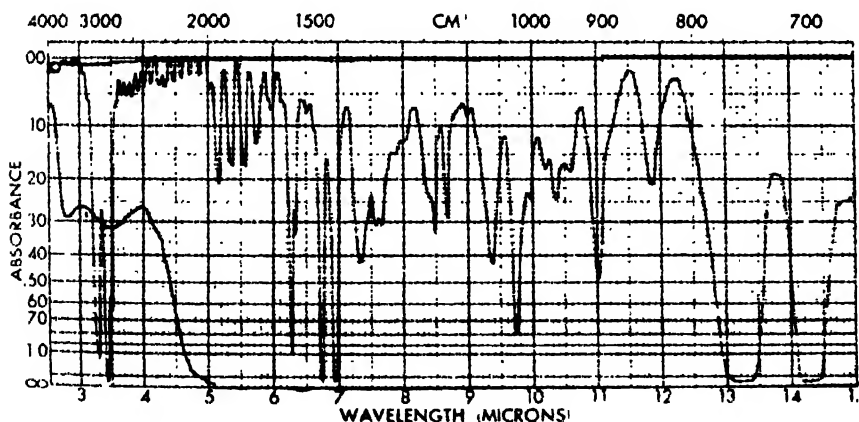


FIGURE 6-1 Recommended instrument performance check: polystyrene, glass (0% T), I_0 (100% T).

Exact procedures for making adjustments vary with the spectrometer make and model, and are adequately described in the instruction manual supplied with the instrument. Correction of inaccuracies in wavelength,

100% and 0% transmission, response, and drift, as well as occasional tube and source replacements present no particular problems, and the chemist can expect to correct these difficulties himself with relatively little effort. Major repairs which require specialized equipment or the knowledge and skill which can only be developed through long experience and training can best be remedied by the service department of the manufacturer or by the instrument group of a large infrared laboratory.

Sample Preparation

A great advantage of infrared spectroscopy as a chemical research tool lies in the fact that the spectra of nearly all substances can be obtained quickly and without elaborate preparation. Highly colored materials, or materials consisting of mixtures of phases, present no particular difficulty. However, because the optical materials that must be used are nearly always crystals of water-soluble materials, such as NaCl, some special although simple techniques must be learned.

Solution Techniques. There are two principal advantages in obtaining spectra in dilute solution: (a) The spectra will tend to be more reproducible, because the surroundings of the molecules (the solvent) are always the same; (b) both qualitative and quantitative analysis may be accomplished with the same spectrum. These advantages are so great as to outweigh some of the disadvantages of solution techniques.

In order to obtain spectra of molecules in solution, a solvent is required which has little or no infrared absorption over a wide wavelength range and is capable of dissolving the material of which the spectrum is required. No single solvent meeting these requirements exists, of course. However, combinations of solvents -- some for use in one wavelength region, others to be employed in other regions -- can be found which will give excellent results in many cases. The most useful solvents in this respect are carbon tetrachloride and carbon disulfide, and a "standard" technique has been devised which employs these solvents in conjunction.

The spectrum is obtained of a 10% solution (i.e., 1000 mg of sample per 10 ml of solution) in CCl_4 in a 0.1 mm cell in the region 2.5 to 7.5 μ , and of a 10% solution in CS_2 in a 0.1 mm cell in the region 7.5 to 15 μ . Use of these solvents in this manner minimizes solvent absorption. Figure 6-2 shows the spectra of pure CCl_4 and CS_2 as obtained in a 0.1 mm cell; it is obvious from the figure why this solvent combination is so useful. Without lengthy discussion, suffice it to say that concentrations of 10% and cell lengths of 0.1 mm have been shown, on the basis of long experience, to be the most practical for general infrared use. This technique is so useful that it should be employed for obtaining all spectra, except for: (a) materials insoluble in CCl_4 — CS_2 ; (b) certain cases in which results are desired very quickly,

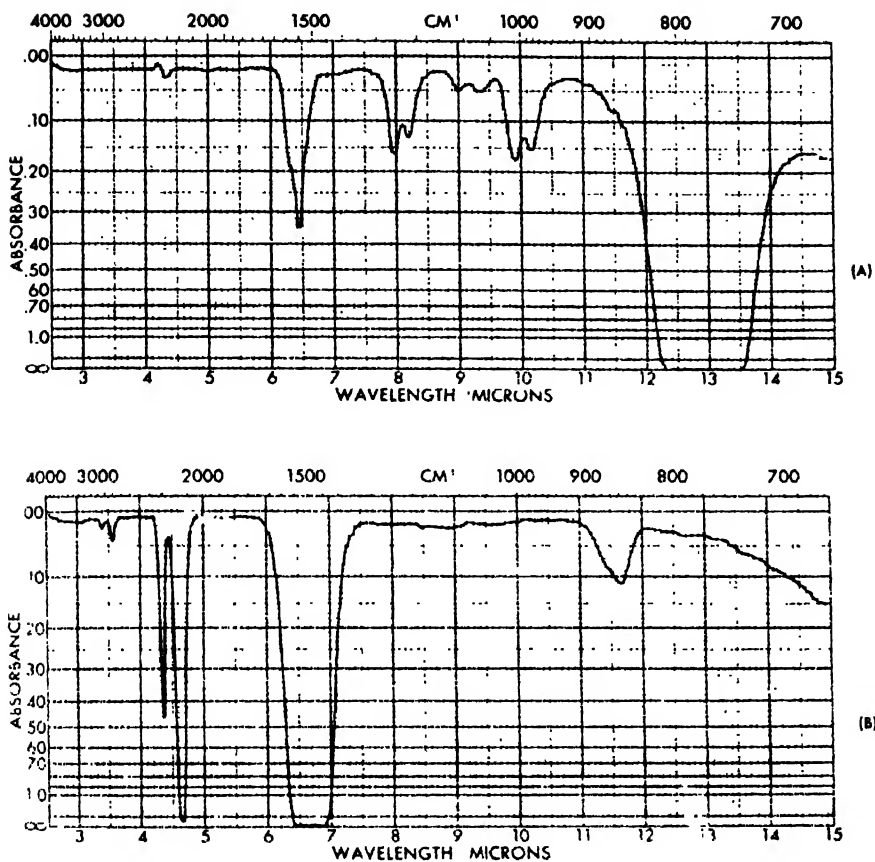


FIGURE 6-2. CCl_4 and CS_2 spectra (0.1 mm). A (CCl_4) and B (CS_2).

and some sacrifice of the quality of the spectrum can be tolerated; (c) special applications, in which it is desirable to obtain the spectra under other conditions (e.g., gases, studies in the solid state, kinetic studies, detection of trace impurities). Examples of these other techniques are described briefly below.

There are other solvents in which infrared spectra may be obtained, but none have nearly as good transparency as CCl_4 and CS_2 . The only purpose in using such other solvents is to obtain solution spectra of polar materials which are insoluble in CCl_4 – CS_2 . Some of the more useful solvents in this respect are chloroform, methylene chloride, acetonitrile, and acetone. Space does not permit elaboration here on the use of polar solvents for obtaining infrared spectra. As a rough rule of thumb we will say that use

of these polar solvents should largely be confined to quantitative analytical applications of polar materials; qualitative analysis of materials insoluble in CCl_4 — CS_2 is probably best done with the non-solution techniques described below.

Cells and Related Optical Materials. The construction, repair, care, and maintenance of absorption cells having NaCl windows, and NaCl plates used in other techniques, presents to the organic chemist perhaps what is the most serious problem of application of infrared spectroscopy. Even with the best of care, rock salt optical parts that are constantly in contact with room air and chemical substances will soon become fogged or etched and hence unusable. Below are given a few suggestions as to how the useful life of these parts may be extended, but the authors are of the opinion that they must be regarded as expendable; results cannot be obtained unless the apparatus is used, and certain applications and inevitable errors will ultimately result in their being rendered unfit for use. Several approaches to this problem exist, all having individual merits:

(a) Excellent quality absorption cells and polished NaCl plates are available commercially in a wide variety of lengths and designs from firms which manufacture infrared spectrometers. These firms will also repair damaged cells and plates, or take them in trade on new equipment. This is the easiest solution of the problem, but it does have one serious disadvantage: expense. The prices for this equipment are not unreasonable, but a large inventory must be kept on hand so that fresh cells and plates are always available while others are away for repair.

(b) At the other extreme, the organic chemist can do all his own optical work. The techniques involved in construction of cells and polishing NaCl plates are not difficult, and have been completely described.¹² However, mastery of these techniques requires some practice and time, and most organic chemists will feel that their time can be better spent elsewhere.

(c) The chemist who is associated with a large academic or government institution, or employed by a laboratory of a large industrial firm, may be fortunate enough to have access to a large infrared laboratory, instrument group, or optical shop which can be persuaded to perform these services for him. This represents the best solution to this problem from his point of view, and he should do all he can to make such arrangements.

(d) A combination of the first two approaches can be invoked: a supply of high quality commercial cells can be kept on hand for precision work, while the chemist can repolish his own rock salt plates used in mull and film techniques (see below).

(e) Inexpensive, expendable cells can be used. A new approach to this problem has recently appeared in the use of the so-called "cavity-cells." These cells are made from a single, small block of rock salt by machining

cavities of appropriate sizes in them by special methods. As their use increases, the price of these cells, particularly in larger quantity, is sure to decrease, so that it may become practical to use such a cell once (or a few times) and then discard it. These cells are available in a variety of sizes and models.

A few remarks on cell care are in order. Cloudy or turbid solutions, or solutions containing suspended solids or liquids, should never be introduced into an absorption cell. If the cloudiness results from traces of water or other highly polar liquids, they can often be cleared up instantly by adding a small amount of granulated NaCl, and decanting the clear solution from the NaCl crystals. If large amounts of insoluble solids are present when the solution is prepared, the solution should be filtered into the absorption cell. During this operation the insoluble solids may be collected, and their spectrum obtained by techniques described below. This latter approach conveniently separates the polar and nonpolar materials in a mixture, thereby facilitating their identification and analysis.

In order to clean an absorption cell it should be flushed with the same solvent used to prepare the solution being used; if some other solvent is used a precipitate may form in the cell which will ruin it. After rinsing well the cell is dried with thoroughly dry compressed air. Room air must not be used for this application, for as solvent evaporates, the inside surfaces of the cell will cool appreciably and condense even small amounts of water vapor, damaging the cell. It will be found that a few cleverly designed gadgets to rinse and dry cells will be well worth while.

Compensation of Solvents. An advantage of the double-beam spectrometer is that it determines the transmission of the material in the sample beam with respect to the reference beam. Thus, any absorption common to both beams will not be observed in the recorded spectrum. This arrangement makes it possible to eliminate troublesome solvent absorptions from the spectrum by introducing a cell containing pure solvent into the reference beam. With this approach, the use of the more polar solvents that have several absorption bands can be extended considerably.

This technique, although useful, must be employed with considerable caution. A very serious limitation in using this technique arises from the fact that in regions of high solvent absorption, little or no light will reach the detector, with the result that the spectrometer is "dead," and the recorded spectrum at this point is meaningless. If the absorption band in the reference beam is transmitting at least 50% of the radiation, there will be sufficient energy to record a reasonably reliable spectrum. However, if the absorption band in the reference beam is transmitting 10% or less of the radiation, the spectrometer cannot be expected to record the difference spectrum faithfully, and no attempt to interpret this region of the spectrum

should be made. In attempting to interpret any compensated spectrum, reference to the spectrum of the pure solvent should always be made to avoid this difficulty.

Film Spectra. The spectra of liquids not soluble in CCl_4 — CS_2 are best obtained for qualitative analysis from capillary films. To do this, a large drop of the liquid is placed between two rock salt plates which are then squeezed together and mounted in the spectrometer in a suitable holder. The plates used in this operation need not have a high polish, but they must be flat; if the plate surfaces are not parallel, a distorted spectrum can result.

This technique has the advantages of rapidity and simplicity, and no solvent absorptions appear in the spectrum. For this reason, it lends itself very well to obtaining quick qualitative information about a reaction or workup while it is in progress. The technique can, of course, be applied to liquids or pastes which are soluble in CCl_4 — CS_2 , and often is advantageous for the reasons just cited. However, if time allows, the CCl_4 — CS_2 solution technique gives better and more consistent spectra, as discussed above.

By slight modification, this technique can be used to obtain spectra of noncrystalline solids (e.g., polymers, resins, amorphous solids) which are insoluble in CCl_4 — CS_2 . The polymer is dissolved in any reasonably volatile solvent, the solution poured onto a rock salt plate, and the solvent evaporated by gentle heating. If the solid is noncrystalline, a thin, homogeneous film is deposited on the plate which can be mounted in the spectrometer and scanned directly. This is one of the most common techniques for obtaining spectra of polymeric materials.

Whether used with liquids or solid noncrystalline films, this technique has the disadvantage that quantitative analysis is not possible directly, because the thickness of the film cannot be precisely controlled. Even in qualitative analysis it is desirable to keep film thicknesses as uniform as possible, and sufficient uniformity for this purpose can be obtained with a little practice.

Spectra of Crystalline Solids. Spectra of powdered, crystalline solids which are insoluble in useful solvents can only be obtained by special techniques. A layer of powdered solid will transmit very little infrared radiation, for the light will be badly scattered by multiple reflections and refractions off the particles. This scattering can be greatly reduced by (1) reducing as many as possible of the particles to a size smaller than the wavelength of infrared radiation, under which circumstance reflection and refraction do not occur, and (2) surrounding the particles by a medium whose refractive index more closely matches theirs, which reduces the reflection and refraction at particle surfaces. Both the major techniques for obtaining infrared spectra of crystalline solids are based on these principles.

The mull technique. The Nujol mull technique accomplishes this by grinding the solid in "Nujol" mineral oil (a purified mixture of alkane hydrocarbons in the range C_{20} – C_{30}) to make a thin paste. The mineral oil serves to suspend the solid while grinding, and acts as a coating about the particles which will match their refractive index more closely than does air. The mull is usually prepared in a smooth agate (or similar hard substance) mortar; when the cream-like suspension is uniform, it is squeezed into a thin layer between flat rock salt plates and mounted in the spectrometer. Excellent spectra can be produced by this technique.

Making a satisfactory mull is somewhat of an art. We have found the following suggestions helpful: (1) Use a large enough mortar and pestle so that a vigorous grinding action can be employed. Some physical labor is necessary in the preparation of good mulls. (2) Use only enough sample to obtain the spectrum; the more sample used, the greater the labor. (3) Use as little mineral oil as possible. (4) Be sure the rock salt plates used are flat (they need not have a high polish). (5) After squeezing the paste between the rock salt plates, check to see that it is at least partly transparent to visible light. If it is completely opaque, a good spectrum usually will not result, and the material must be reground. After sufficient practice, a good mull can be made of most solid materials in just a few minutes.

Alkane hydrocarbons have a strong absorption at $\sim 3.4\mu$, and somewhat weaker absorptions at $\sim 6.8\mu$ and $\sim 7.3\mu$. If these absorptions will interfere with the spectrum to be obtained, a second mull can be made using a non-hydrogenous oil, as perfluorokerosene. If the perfluorokerosene mull is scanned from 2.5 to 7.5μ , and the mineral oil mull is scanned from 7.5 to 15μ (analogous to the use of CCl_4 and CS_2 solvents), interfering absorptions from the mulling agents will be minimized.

Pressed disk technique. The pressed KBr technique consists of intimately mixing a few milligrams of the crystalline sample with 500 mg of specially purified KBr, and compressing the mixture into a disk at 500 to 1000 atmospheres pressure. KBr becomes quite plastic at high pressure, and will flow to form a clear disk.

The grinding-mixing operation is probably most conveniently done in a vibrating ball mill, such as used by dental technicians for preparing amalgams. Suitable dies in which the pellet can be pressed are available from manufacturers of infrared equipment. Any laboratory press capable of delivering the required pressure will serve.

Because of the rather expensive equipment involved, organic bench chemists will probably prefer the mull technique. We have not space here to debate the relative merits of the two techniques; suffice it to say that the mull technique will prove very satisfactory for the great majority of samples with which the organic chemist will be concerned.

QUALITATIVE ANALYSIS

The "Fingerprint" Concept

Applications in Synthesis. The infrared spectrum is highly sensitive to changes in molecular structure. The vibrational frequencies of a molecular

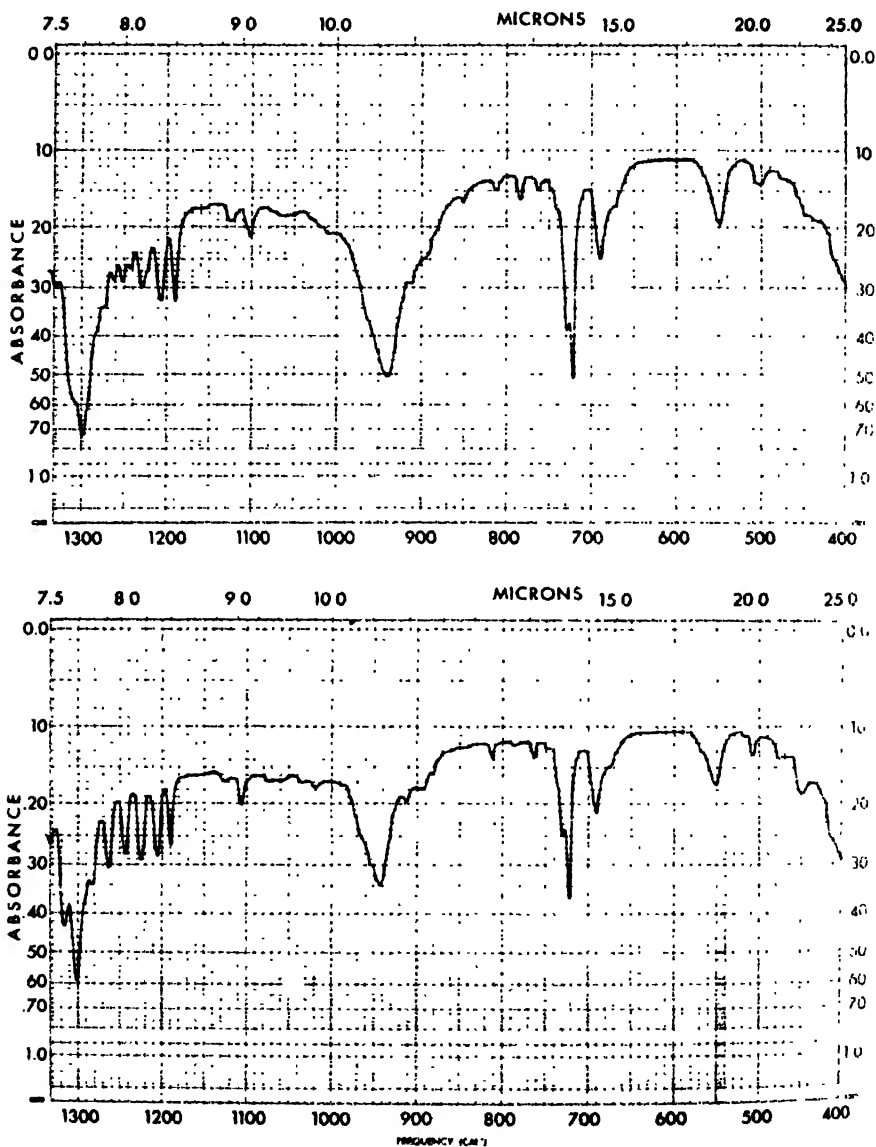


FIGURE 6-3. Crystalline stearic acid as obtained from two different suppliers.

system are altered if changes are effected in (1) the mass of the atoms, (2) spatial arrangement as in *cis-trans* isomerism or in changing from a branched to straight chain or (3) bond strengths. As a consequence the infrared spectrum is a much more characteristic property than the refractive index, density, melting point, or boiling point.

This "fingerprint" nature of the infrared spectrum provides positive evidence for proving or disproving identity of two substances by comparison of their spectra. This can be invaluable in synthesis. Starting materials, solvents and known products can be immediately identified when isolated from reaction mixtures without resorting to the time-consuming preparation of derivatives or the less positive identification obtained by conventional physical constants. This technique is especially useful for identification of substances which decompose below their melting points.

The infrared spectrum is so specific that frequently different crystalline forms of the same compound will, in the solid state, show different spectra (see Figure 6-3). For this reason, when comparing spectra for identity, it is recommended that, where possible, solution spectra be employed. For a more complete discussion of the physical and chemical factors affecting the spectra of solid substances the review by Duyckaerts⁷ is recommended. The factors discussed include polymorphism, mixed-crystal formation, distortion of crystalline structure, formation of complexes between substance and medium, adsorption of substance on particles of dispersing medium and actual chemical reactions of the substance with the medium.

A minor specificity limitation exists in the infrared spectra of compounds differing only by the addition of a group already present in large numbers. Thus it is difficult to detect any differences in the spectra of the molecules $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ where n is changed, for example, from 16 to 18.

It is nearly always possible to distinguish between compounds having different geometrical structures or different functional groups. Thus the spectra of isopropyl alcohol and *n*-propyl alcohol or *o*-, *m*-, and *p*-dichlorobenzene are characteristically different (see Figure 6-4). Not only do differences exist in the spectra of such isomeric materials but the differences are predictable so that structural assignments may be made with the help of group frequencies to be discussed shortly.

Cis-trans isomerism. It is often possible to assign a *cis* or *trans* configuration on the basis of infrared spectra, particularly when both isomers are available. In a symmetrically substituted case such as *cis* and *trans* dibromoethylene (Figure 6-5) this assignment is simple because the ethylenic double bond stretching mode of the *trans* isomer undergoes no dipole moment change with vibration and thus will have no infrared absorption.*

* The weak absorption at 1635 cm^{-1} in the *trans* isomer results from a combination band; the $\text{C}=\text{C}$ absorption of the *cis* isomer at 1585 cm^{-1} shows considerably more intensity.

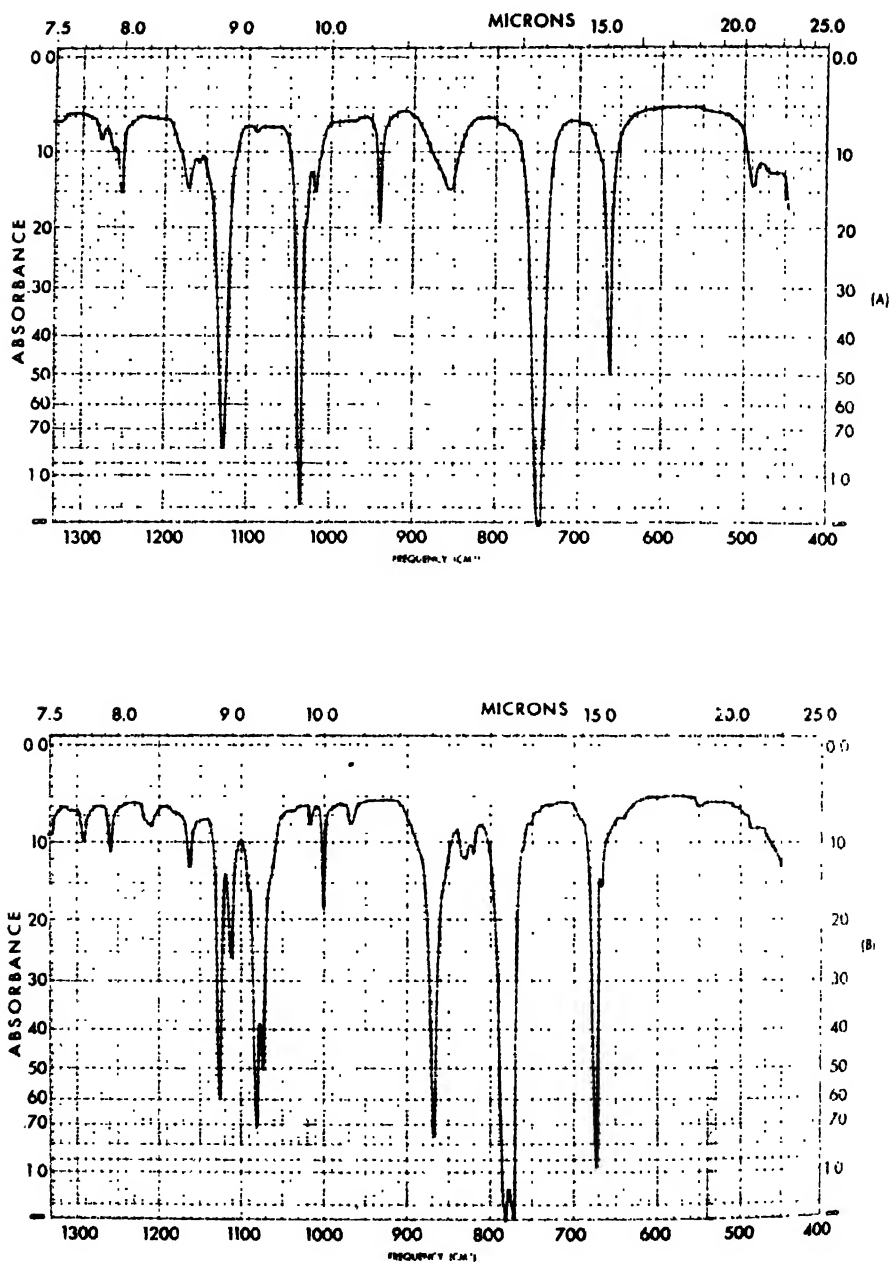


FIGURE 6-4. Infrared spectra of dichlorobenzene isomers: (A) *ortho*; (B) *meta*; (C) *para*.

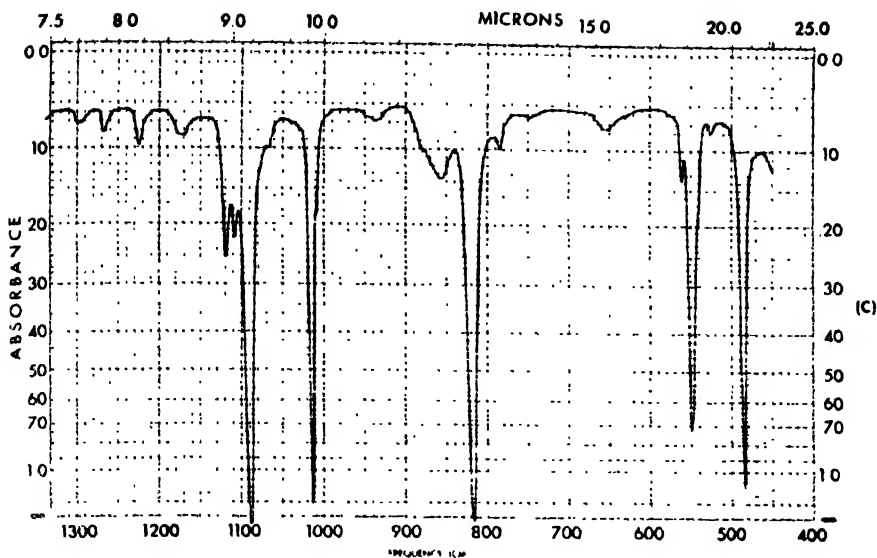
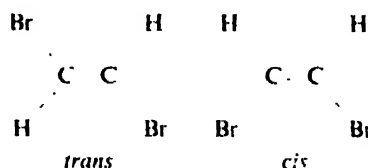
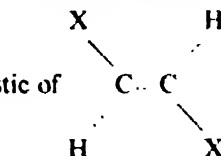


FIGURE 6-4. Cont'd

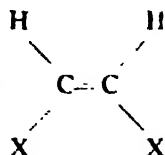


On the other hand, the *cis* isomer has no such center of symmetry and will show a characteristic ethylenic double bond absorption at 6.51μ (1585 cm^{-1}). An even better differentiation between *cis* and *trans* isomers is available from the out-of-plane hydrogen deformation bands: the strong absorption

at 11.11μ (900 cm^{-1}) is characteristic of



at 14.93μ (670 cm^{-1}) results from



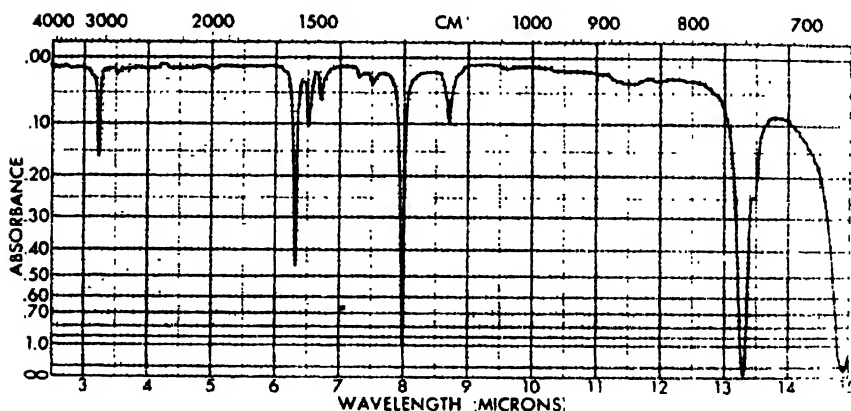
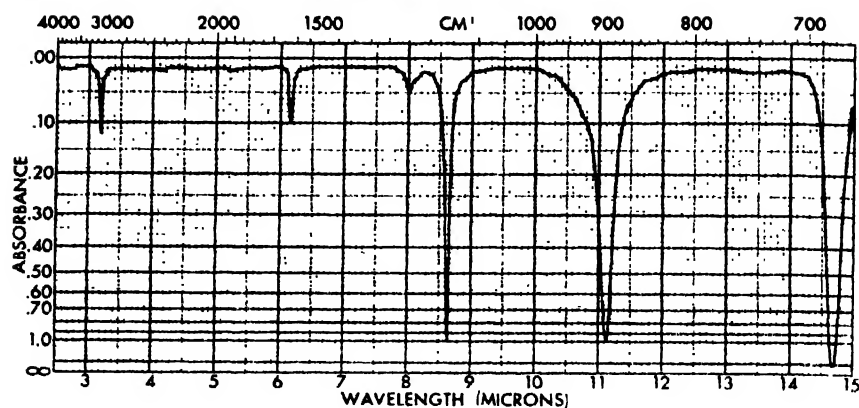
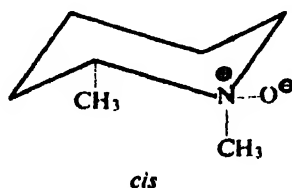
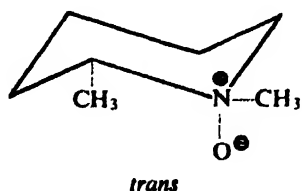


FIGURE 6-5. Infrared spectra of *cis* and *trans* dibromoethylenes: (A) *trans*, (B) *cis*.

In more complicated cases not involving the ethylenic double bond such as the *cis-trans* isomerism of *N*-methyl- α -pipercoline oxide studied in detail by Cope and LeBel,⁵ it is significant to note the nonidentity of the spectra of the two isomers even though certain functional group bands are common to both.



Optical isomerism. Because enantiomorphs are mirror images of one another, their spectra in the gaseous, liquid, or solution phases are identical. Thus infrared solution spectroscopy has been useful in demonstrating the identity of an unresolved synthetic compound with that obtained from natural sources. For reasons previously discussed, the spectrum of a single enantiomorph in the solid state will exhibit differences from that of the racemate, for the crystalline forms are different. Diastereoisomers, on the other hand, will exhibit differences in spectra regardless of physical state.

Keto-enol tautomerism. The reactivity of certain compounds may be explained by keto-enol tautomerism. Infrared examination of 2-hydroxypyridine, for example, shows that it exists nearly exclusively in the keto

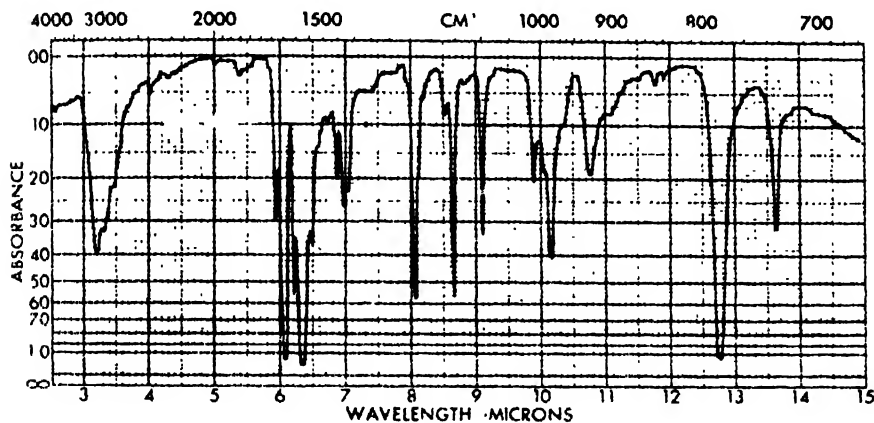
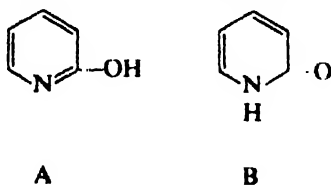
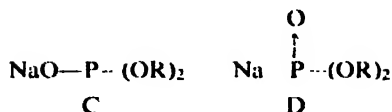


FIGURE 6-6. 2-Hydroxypyridine:fluorolube · Nujol Mull.

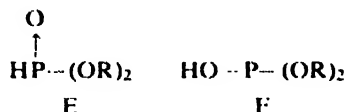
form (B) in neutral solution or in the solid state and not in the enol form (A); actually it reacts with methyl iodide under neutral conditions to give N-methylation. The spectrum of 2-hydroxypyridine is shown in Figure 6-6.



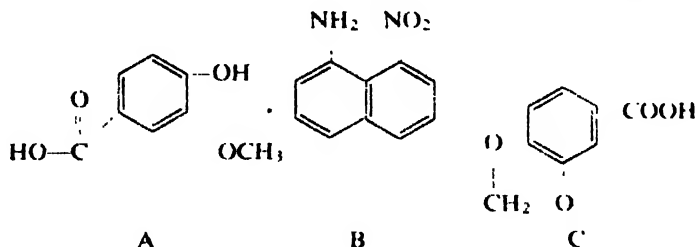
The mode of reaction of sodium salts of dialkyl hydrogen phosphites in the Nylen reaction was elucidated⁶ when it was shown by infrared that the sodium atom was attached to oxygen as in structure C and not directly to phosphorus (structure D) as was previously supposed.



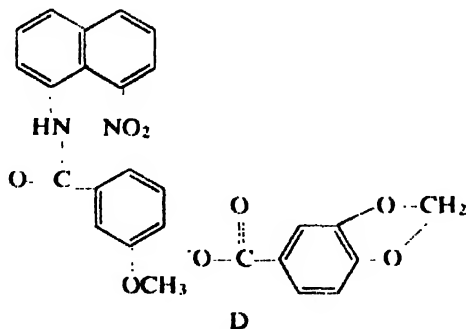
It was shown also that the free dialkyl hydrogen phosphites did exist in the commonly accepted "keto" form (E) with a negligible contribution from the "enol" (F).



Complex molecules. Identification of complex molecules by infrared can sometimes be facilitated by degradation of the molecule and identification of the fragments. As a hypothetical example, let us assume that a new antiviral agent has been discovered in a fermentation liquor. The compound has been isolated and purified and its infrared spectrum shows the presence of aromatic rings with varied substitution patterns, as well as amide, ester, nitro and alkoxy functional groups. Recognizing that amides and esters are subject to hydrolysis, this is carried out and three components (A, B, and C) isolated and identified by comparison with known spectra.



The final proof of structure may then be obtained by recombining the three components, forming a compound (D) with an infrared spectrum identical with the original.



Determination of Purity. In addition to proof of identity or nonidentity, infrared is frequently useful for a qualitative check on purity. By comparison with a standard spectrum the presence of impurities in a sample may be readily detected by the appearance of additional absorption bands. When abnormalities in synthesis are encountered it is particularly valuable to determine quickly the purity of starting materials and solvents. When starting materials are known to be subject to hydrolysis or if their stability or identity is in any way subject to question, much time can be saved by obtaining an infrared spectrum before carrying out a reaction.

Purity may be checked qualitatively when reference spectra are unavailable. A spectrum consisting of sharp, well-defined bands as a general rule is characteristic of a pure compound, whereas impure materials will often show more numerous, less well-defined bands. Furthermore, in many cases impurity bands may appear in regions (e.g., carbonyl or hydroxyl) where the compound in question is known to be devoid of absorption.

Publication of Spectra. In order for the chemist to utilize fully the advantages of identification by infrared "fingerprinting," it is necessary to have available published spectra of the widest variety of compounds. Ideally the publication of each new chemical should include its infrared spectrum; this would in many cases be more useful than its published melting point or boiling point, for the infrared spectrum would not only serve as a means of comparison for identity but would also be useful as an indication of purity. Unfortunately, the ever-increasing quantity of chemical literature has forced most journal editors to adopt policies which favor brevity even at the expense of usefulness. Thus the chemist must rely nearly exclusively on spectral catalogs and books on infrared for standard spectra. These are discussed below.

The existence of the spectrum of a chemical firmly affixed to the chemist's notebook is the very best patent evidence that the compound described was actually prepared. Likewise, considerably more use of spectra could be made in patents to describe positively the claimed composition of matter. In addition to increasing the definition of the invention, such a spectrum in a patent would be available as a reference standard for subsequent workers in related fields.

Interpretation of Infrared Spectra: The Group Frequencies

Perhaps the most appealing feature of infrared spectroscopy from the point of view of organic chemists is the existence of the so-called "group frequencies." Specific functional groups, as OH , $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, etc., often have one or more vibrational modes which are for the most part reasonably constant and essentially independent of molecular structure, and whose resultant infrared absorption bands tend to occur in narrow, characteristic regions of the spectrum. Such an absorption band is often spoken of as a

"group frequency," as its presence in the infrared absorption spectrum is evidence for the specific functional group. However, not all infrared absorption bands are group frequencies, as we shall see.

To be useful as an indication of a specific functional group, an absorption band must: (1) have its frequency essentially independent of the molecular environment of the specific functional group; (2) or, if it does show frequency variation with variation of adjacent structure, this must be correlatable with some chemical property of the adjacent structure; (3) be somewhat uniformly intense with respect to other absorption bands that may occur in the same frequency region. Absorption bands which have these properties are obviously extremely useful, for in the simpler limiting cases one relatively easily obtained piece of data --- the infrared absorption spectrum --- tells at once what functional groups are present or absent in a molecule. Furthermore, if the functional group meets the condition (2) above --- if the frequency variation of its characteristic absorption can be correlated with structure --- this very property can often give most valuable additional information.

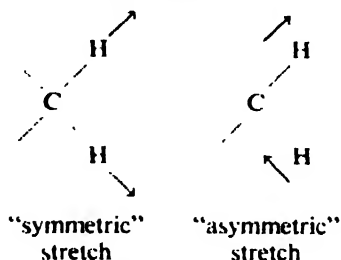
When are absorption bands good group frequencies and when are they not? There is no direct and simple *a priori* answer to this question; experience has shown that some will be found to be highly reliable, others will be observed to be of little utility. Space does not permit elaboration of this point here, except to say that as a rather rough generality, the vibrations which are composed principally of stretch of a heteropolar bond, or certain hydrogen bending motions constitute the majority of the useful group frequencies, while other vibrations are not so useful.

Classification of the Group Frequencies. In order better to understand the classifications and listings of group frequencies in the literature, which we shall discuss below, it seems worthwhile to pause here and describe some of the persistent vibration motion types that constitute them. The major classes that form useful group frequencies are: hydrogen stretch, hydrogen bend, single-bond stretch, double-bond stretch, and triple-bond stretch. It should be recognized that hydrogen, because of its low mass, is a unique element, and many vibrations involving hydrogen motions are essentially just that: they do not involve much motion of the heavier elements to which they are bonded. On the other hand, vibration of the "heavy elements" (i.e., carbon and heavier) are not so simple, but often involve considerable motion of other atoms. We shall elaborate on this a bit further below.

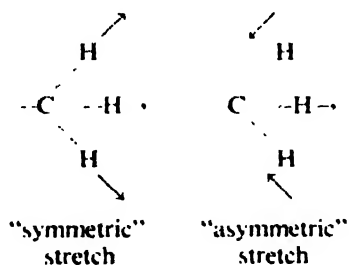
A hydrogen stretching (str) vibration of a single proton bonded to a central atom, as, $\text{O}-\text{H}$, $\text{X}-\text{H}$, $\text{>N}-\text{H}$, ---C---H , is simply the motion of the proton alternately toward and away from the central atom:



If there are two hydrogen atoms bonded to the same central atom, as CH_2 , NH_2 , or OH_2 , there are two hydrogen str motions:



Because these motions are different from each other and from the vibrational motion of a single hydrogen atom, the frequencies of all three are slightly different, even though the forces between atoms are very similar. However, these differences are slight: all alkane C-H stretches, for example, tend to fall in a relatively narrow frequency region. If there are three hydrogen atoms bonded to the same central atom, as $-\text{CH}_3$, NH_3 , there again are two hydrogen str motions:



(Actually, there are two possible asymmetric str motions in this case, but they have the same vibrational energy and frequency, and hence absorb at the same frequency. The only difference between the two motions is one of mathematical formalism; when two different molecular vibrational motions have identical frequency they are said to be degenerate.) Again, these frequencies are slightly different from the cases of two protons or a single proton bonded to the same central atom.

Although there are slight differences between hydrogen str frequencies as a result of the geometry about the central atom, by far the greatest influence on these frequencies results from the identity and valence type of the central atom. For example, O---H bonds are usually stronger (i.e., have higher heats of formation) than C---H bonds, thus have higher force

constants, and hence O-H str frequencies will generally be greater than C-H str frequencies. Because the chemical bonds formed by hydrogen atoms to most other elements are reasonably strong, and thus have fairly high force constants, but more particularly because the mass of the hydrogen atom is so uniquely low, the great majority of the hydrogen str vibrations fall at the high frequency end of the fundamental region: 2.5μ (4000 cm^{-1}) to 4μ (2500 cm^{-1}). Specific frequency regions for the various hydrogen str vibrations are summarized on the correlation chart below.

Hydrogen bending motions also constitute a large share of the observed absorption bands in the infrared spectrum. Only certain classes of these vibrations make useful group frequencies, however. Without discussing this point in detail, we may say that in most cases useful group frequencies

H

result from internal hydrogen deformations (i.e., those in which the Y-H angle changes), and out-of-plane hydrogen deformations (those in which the hydrogen motion is perpendicular to a planar structure, as ethylenic or aromatic); on the other hand, hydrogen skeletal deformations (those in which the principal motion is that of hydrogen but with little or no change

H

in the Y-H angles), and in-plane hydrogen deformations (those in which

H

hydrogen motion is strictly in the plane of an ethylenic or aromatic system) are usually not considered to be useful group frequencies. The principal reason for this is that internal hydrogen deformation and out-of-plane hydrogen deformation vibrations are usually nearly pure hydrogen motion, while hydrogen skeletal and in-plane hydrogen deformation vibrations are usually tightly coupled to motions of other atoms.

Vibrations that are the result of bending motions of atoms heavier than hydrogen are rarely observed in the region of the spectrum covered by the spectrometers usually employed by chemists (2.5 to 15μ). The force constants of bending motions are low, and therefore only the bending motions of the uniquely light hydrogen atoms are of great importance to chemists. Internal hydrogen deformations tend to occur in the region 6 to 8μ ; out-of-plane hydrogen deformation absorptions are found in the region 10 to 15μ . These frequencies are of great value in determining structure types; in particular, the out-of-plane hydrogen deformation vibrations can be used to determine the position of substituents on aromatic rings and ethylenic C=C bonds. The useful correlations of hydrogen deformation frequencies with chemical structure are summarized on the correlation chart below.

For atoms heavier than hydrogen (principally carbon, nitrogen and oxygen) only the str vibrations are important. These frequencies would be expected to be observed at considerably longer wavelength than hydrogen str frequencies, and this is indeed true for single bond str vibrations. However, carbon is capable of forming multiple bonds, which hydrogen is not, and, as might be expected, multiple bonds have larger force constants than single bonds, with the result that multiple bond str vibrations of the elements of the first row of the periodic table also occur toward the higher frequency end of the vibration spectrum.

Of these, the triple bond str vibrations will have the highest frequencies, of course. The motion involved in these vibrations is somewhat different from hydrogen str, for here both atoms of the stretched bond, being of comparable mass, move approximately the same: $\overleftrightarrow{\text{C}\equiv\text{N}}$. Another type of vibration found in the same frequency region as triple bond stretch is the asymmetric str vibration of allenic carbon systems: $\text{C}=\text{C}=\text{C}$.

Other examples are $\text{C}=\text{C}=\text{O}$, $\text{C}=\text{N}=\text{C}=\text{O}$, $\text{N}=\text{C}=\text{S}$. Here the motion is simply described as: $\overleftarrow{\text{C}}-\text{C}=\overrightarrow{\text{O}}$ where the central carbon atom moves back and forth between the terminal atoms to each of which it is attached by a double bond. Symmetric str modes of these systems: $\overleftarrow{\text{C}}=\text{C}=\overrightarrow{\text{O}}$ absorb at considerably lower frequency, and are not generally regarded as useful group frequencies. In summary, triple bond str modes, and asymmetric str modes of allenic carbon groups, fall in the frequency region of 4.3 to 5.1μ (2300 to 1900 cm^{-1}) (see correlation chart below).

Double bonds, as would be expected, have somewhat lower force constants than triple bonds, and therefore their str vibrations occur at lower frequencies: 5.4μ (1850 cm^{-1}) to 7μ (1400 cm^{-1}). Of these vibrations, the $\text{C}=\text{O}$ str absorption is by far the most useful, for it nearly always produces a very intense absorption band (high dipole moment change with stretch), and the exact frequency is a very sensitive function of the nature of the groups attached to the carbonyl carbon atom. The literature on just this single group frequency is vast; space does not permit a discussion of these correlations here, but the more important ones have been summarized on the correlation chart below, and extensive discussion can be found in the standard texts cited.

Carbon-carbon double-bond str vibrations, by contrast, are not nearly so useful, for their intensities are often very low, in some cases being identically zero. The str vibrations of $\text{C}=\text{C}$ groups whose substituents are hydrogen atoms or nonpolar carbon atoms give rise to weak absorptions in the region

6.0 to 6.3 μ . On the other hand, if one of the substituents is a highly polar atom or group (oxygen, halogen, carbonyl), the absorption band falls in the same region, but can be quite intense.

The range of C=C str frequencies in cyclic systems, particularly aromatic rings, is much broader, because the actual forms of the vibrational motions are much more complex than just simple elongation of one C=C bond, and there are several such motions possible. Aromatic systems in general will show one or more intense absorptions in the region 6.2 to 7.3 μ , but the frequency and intensity vary enormously with the nature and (especially) the position of the substituents. However, presence of one or more strong, sharp bands in the region 6.6 to 7.0 μ is one of the best indications of aromatic ring structure (see correlation chart).

The absorptions that result from vibrations which are principally single bond str motions fall at yet lower frequencies, as we should expect. The range of different single bond str frequencies is very broad: 7.5 to 20 μ . This is so for several reasons: (1) Single bonds can vary widely in their character; for example, the C—O bond in phenol is certainly stronger than the C—O bond in benzyl alcohol. (2) The forms of the vibrations are much more complex than for hydrogen str or multiple bond stretching vibrations; the vibrations which involve str of the C—O bonds in diethyl ether, for example, also involve other motions of adjacent groups. (3) Many of the single bonds in which the chemist is interested are those of atoms considerably heavier than carbon, nitrogen, and oxygen; vibrations of heavier atoms, of course, occur at lower frequencies. For these reasons, then, the single bond str frequencies, although very useful, do not constitute as useful a class as do the other vibration types discussed.

The str vibrations of chemical bonds of the coordinate covalent type (or

so-called "ion-dipolar" bond, or "dative" bond), as $\begin{array}{c} | \\ \text{---P---O,} \\ | \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \text{S} \diagup \diagdown \\ \diagdown \diagup \end{array}$ $\begin{array}{c} \text{O} \\ \diagdown \\ \text{O} \end{array}$,

etc., do produce useful group frequencies. They are particularly useful because these frequencies are very sensitive to inductive effects of adjacent groups, and thus not only make it possible to identify, say, —SO₂— groups, but also make it possible to characterize them further as sulfonate, sulfone, sulfonamide, etc. These characteristic frequencies are summarized on the correlation chart.

Other useful single bond str frequencies are those of the single bonds of the carbonyl carbon atom, and C—O bonds. Both of these classes produce some of the strongest infrared absorption bands in the spectrum. However, the str vibrations of C—S, C—C, and C—N bonds do not produce very useful group frequencies because their absorption bands are often very weak.

The other types of single bond str vibrations (P—O, S—O, N—O, C—halogen, etc.) are not easily classified. Some give rise to good group frequencies, some do not. Skill in interpretation of these bands can only be gained through wide literature knowledge, or experience.

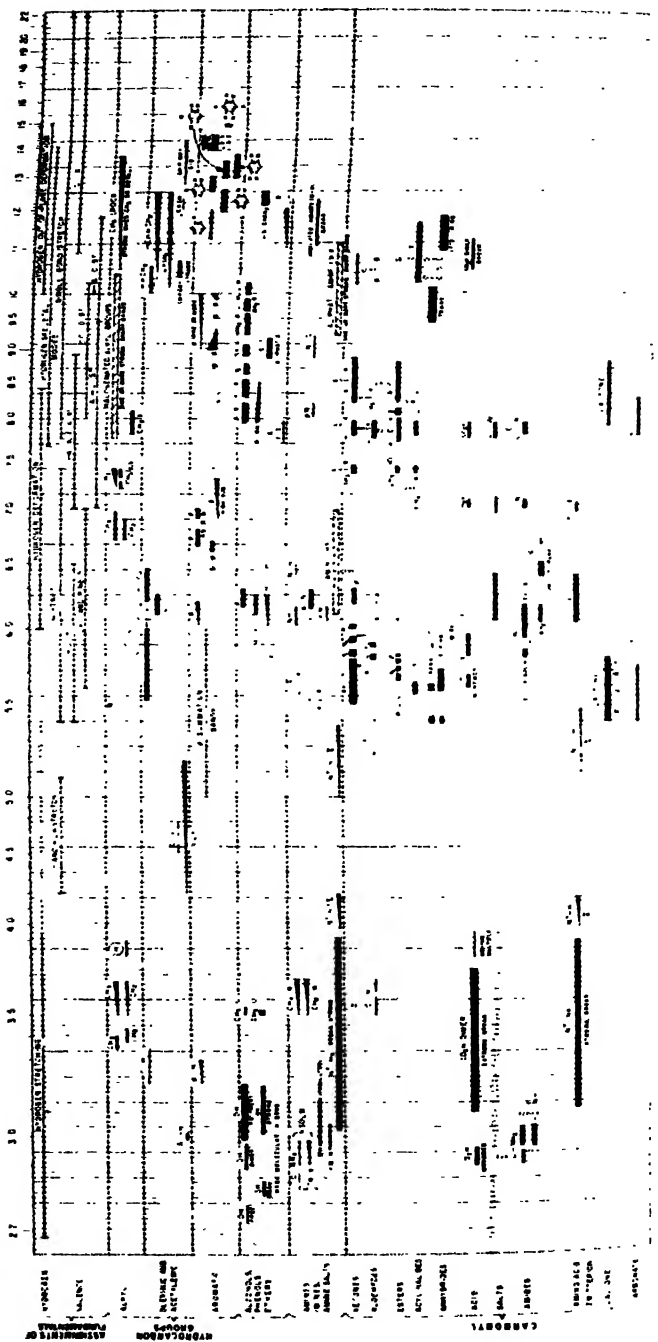
A Correlation Chart. One of the most convenient ways to refer to the specific group frequencies is through the use of a correlation chart. Many such charts have been prepared by various authors, perhaps the best known one being that due to N. Colthup.⁴ Figure 6-7 shows a similar type of chart, which has been prepared on a wavelength scale.

An important feature of this chart is the classification of the frequencies into broad general types (essentially a summary of the preceding material). Appreciation of these classifications is essential in the intelligent application of group frequencies. Often, compounds will be synthesized containing groups whose characteristic infrared absorption frequencies have not been studied, and a knowledge of these frequency classifications will prove most helpful in their interpretation: a strong absorption in the region of 3.7μ *must* result from hydrogen str; a strong absorption in the region 6.6μ *must* result from double bond str or internal hydrogen deformation; use of these classifications can thus prevent absurd errors of band assignments.

We have attempted to indicate both the frequency region and the approximate intensity of the group frequencies. The length of the short, heavy line under each group symbol indicates the extremes of the frequency region in which such groups are known to have a characteristic absorption. The thickness of the line is a rough index of the intensity of this absorption. A line of tapering thickness indicates the intensity for this group to be quite variable. An open, cross-hatched line represents a region in which there is usually more than one absorption band characteristic of a particular structure type; for example, halogenated alkane hydrocarbons often have several strong, sharp absorptions in the region 7.5 to 10.5μ , to which it is difficult to ascribe specific vibrational motions, but which nonetheless are characteristic of that class of molecules.

The chemical symbols are those of standard organic nomenclature. A few, perhaps, should be amplified: X = halogen *except* fluorine; M = metal; N—H = hydrogen attached to a positively charged nitrogen atom, as in amine salts; Σ = a "summation" band - i.e., a combination or overtone, *not* a fundamental; ϕ = phenyl ring; C' = conjugated.

It must be emphasized that a chart such as this, although useful for reference, can be misleading without at least some understanding of the behavior of infrared absorption bands with structure variations. This knowledge can be obtained either through experience or careful study of comprehensive texts on the subject. On the other hand, many of the principal



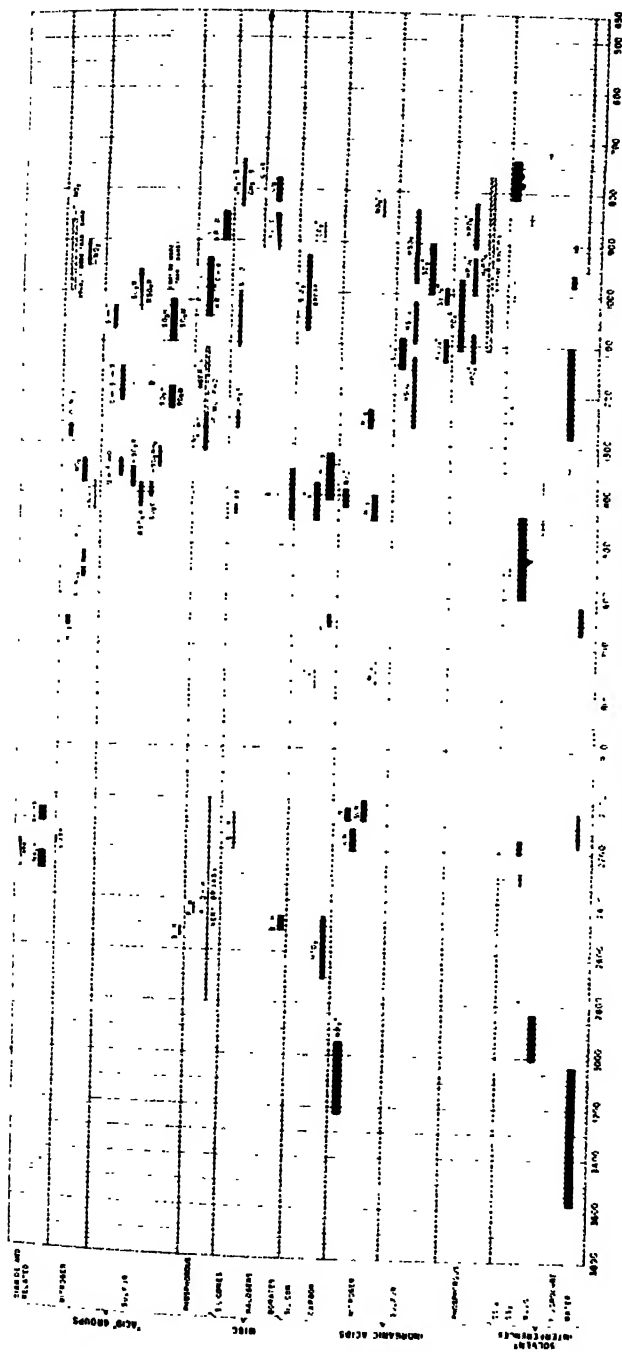


FIGURE 6-7. Group frequency correlation chart.

infrared band correlations, as, O—H stretch, C=O stretch, ϕ —O stretch, along with many others, require no great skill in interpretation in the majority of cases, and an organic chemist can place a great deal of reliance in them with only modest experience. For example, no expert knowledge of interpretation of infrared spectra is required to determine if a CO₂H group has been esterified, or if an allylic rearrangement has occurred, or if a C=C bond has formed as the result of dehydrobromination, and the time required to obtain these data is small, as discussed earlier in this chapter. Therefore, though it is to be used with caution, the infrared spectrometer with the correlation chart of Figure 6-7 can be among the most useful analytical tools the organic chemist can have at his disposal. The more this technique is used, the more useful it will prove to be.

A Short Guide to the Infrared Literature

As has been stressed above, skill in interpretation of an infrared spectrum can only be attained through a reasonable knowledge of the behavior of the group frequencies. The literature on this subject is vast; an attempt to acquire sufficient information from the original literature would be a most tedious undertaking. Fortunately, excellent texts on this subject, conveniently summarizing the existing literature up to the date of their publication, have been prepared. Perhaps the best known and most widely-used texts in the English language are: L. Bellamy, "The Infrared Spectra of Complex Molecules," second edition, Methuen and Co., Ltd., London (1958); and R. N. Jones and C. Sandorfy, "The Application of Infrared and Raman Spectroscopy to the Elucidation of Molecular Structure," in "Techniques of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York (1956).

Bellamy's text is particularly convenient for the organic chemist. It has been arranged by chapters, each of which deals with the characteristic infrared absorptions of a limited class of functional groups. This makes reference to the absorptions characteristic of a particular functional group a relatively simple matter. This text is essentially a very thorough condensation of the literature on group frequencies as known at the time of its publication, and copious references to the original literature are given.

Jones and Sandorfy contains much the same information as Bellamy, also well referenced. In addition, it contains information on other aspects of infrared spectroscopy: instrumentation, sampling methods, quantitative analysis. Also, the characteristic Raman frequencies of each group are discussed. Because this work is but one chapter in a large book on various branches of spectroscopy, reference to characteristic frequencies of a specific functional group is not quite as convenient as with Bellamy's text, but nonetheless this text is most valuable for reference, and should be used.

A word of warning about using such texts as these is in order. Some experience in interpretation of infrared spectra is necessary in order to avoid being misled. This is not the fault of the texts: both have been prepared in a careful manner, with appropriately qualifying statements concerning the behavior of the characteristic absorption bands under discussion. But beginners in this field must be made aware that it is simply not possible in all cases to be sure that a particular absorption band observed in the spectrum arises from the group that is suspected, for many regions of the spectrum will be populated by absorption bands from more than one possible functional group. For example, two very common errors made by beginners are: (a) a tendency to assign a sharp band in the region 7.2 to 7.3μ to symmetrical methyl deformation (other absorptions, especially resulting from highly substituted aromatic rings, alcohols and ethers often occur here); (b) assignment of the weak C—O first overtone absorption that occurs at $\sim 2.9\mu$ to traces of OH impurity. Errors in interpretation can best be minimized through experience; similarly, the more experience acquired in interpreting infrared spectra, the greater will be the confidence in the method.

From time to time review articles have appeared in *Analytical Chemistry* which have summarized the literature on the analytical aspects of infrared spectroscopy appearing since the last article. These articles are particularly useful for keeping abreast of recent work on the group frequencies, whose literature has become so voluminous. The more recent ones are by R. C. Gore: *Anal. Chem.* **26**, 11 (1954); **28**, 577 (1956); **30**, 570 (1958); **32**, 238 (1960) and by J. C. Evans: *Anal. Chem.*, **34**, 225R (1962); **36**, 240R (1964). Presumably similar reviews will continue to appear in *Analytical Chemistry*, probably biennially, or nearly so.

The infrared spectra of many thousand chemical compounds have appeared in the literature, but, until recently, the task of locating them, while not insurmountable, has proven far too difficult to be useful for quick reference for analytical applications. Fortunately, this situation has been corrected with the appearance of an index by H. Hershenson: "Infrared Absorption Spectra: Index for 1945-1957," Academic Press, New York (1959); Vol. II for 1958-1962 (1964). Volume I lists approximately 7,000 compounds alphabetically with literature references to their published infrared spectra, and makes it a simple matter to locate infrared spectra quickly in the periodical literature. Volume II contains about 20,000 references to infrared absorption spectra.

The American Society for Testing and Materials (ASTM) published an index, ASTM Special Technical Publication No. 331, Philadelphia (1962), to 43,500 infrared spectra listed on Wyandotte-ASTM punched cards between 1951 and 1960. The sources of the spectra were the general literature, and collections issued by the American Petroleum Institute, the

National Bureau of Standards, the Sadtler Research Laboratories, the Coblenz Society, D.M.S., the IR Data Committee of Japan, and the Manufacturing Chemists' Association. Supplements to the index are promised.

The most convenient reference for a chemist making extensive use of infrared spectroscopy is a catalog of reference spectra that he can keep near the spectrometer. Such catalogs are commercially available, but any reasonably complete one will be rather expensive when compared to the price of the "tabletop" spectrometer. Perhaps the best approach in this respect is for the organic chemist to assemble his own. Normally his research effort will be directed along a relatively limited class or classes of organic compounds, and in many cases he can assemble the pertinent spectra himself as his research progresses. In addition to compounds specific to his own research work, his catalog should include as many common reagents and solvents as possible, for quick check on the identity and purity of starting materials and solvents, as discussed above, can be a priceless saver of time. If several chemists make use of the same spectrometer, a cooperative effort in this respect should prove invaluable.

QUANTITATIVE ANALYSIS

Principles of Quantitative Analysis

Another of the great advantages of infrared spectroscopy is the ease with which approximate quantitative analysis can be performed. The high specificity of an infrared absorption spectrum provides a powerful method for the determination of the quantity of several components in a relatively complex mixture. When used with experience and judgement, the methods of infrared spectroscopy usually give a high degree of confidence that the measurement being made is proportional to one specific component, and that small amounts of unknown or unsuspected components will not interfere with it. This, of course, offers an enormous advantage over the more classical methods of refractive index, density, pH, etc.

There are certain limitations in quantitative analysis by infrared methods of which the organic chemist should be aware. Existing infrared spectrometers are energy limited; in order to achieve reasonable compromises between resolution, scan time, and signal-to-noise ratio, the spectrometer must be operated near the limit of its capabilities. This emphasizes the need for strict and regular testing programs (such as discussed above) in order to insure correct performance. However, if the spectrometer is carefully maintained, and careful experimental technique employed, reasonably good results can be obtained quite expeditiously.

In order to perform highly precise quantitative analysis by infrared methods, somewhat more care, knowledge of theory, and expense for equipment

than the organic bench chemist is usually willing to expend are required. Therefore, we shall discuss quantitative analysis from the point of view of practical synthetic organic chemistry: what is the yield? -- how much starting material remains? what are the identity and approximate composition of this distillation cut? etc., and leave problems of high precision in analytical determinations to the professional analytical spectroscopist. The present "tabletop" spectrometers are eminently satisfactory for the organic chemist's practical problems.

The functional relationship between light transmitted by a chemical mixture containing an absorbing component and the concentration of the component in the mixture is the well-known Beer's law: $T = \frac{I}{I_0} = 10^{-abc}$, where I is the light intensity transmitted by the sample, I_0 is the light intensity incident upon the sample; the ratio I/I_0 is T , the fraction of incident light transmitted by the sample. The length of the absorption cell is b , the concentration of the absorbing molecule is c ; a is a constant depending only upon the identity of the absorbing molecule and the wavelength of light being absorbed -- it is usually called the *absorptivity* of the molecule at a given wavelength, and its units depend on those chosen for cell length and concentration.

It must be remembered that what the infrared spectrometer actually measures is T , and this is not related in a convenient way to concentration, which is what we wish to measure. However, by printing the spectrometer chart with a suitable scale, a number can be obtained which will be directly proportional to concentration. This is done by defining a quantity called the *absorbance*:

$$A = -\log_{10} \frac{I}{I_0} = \log_{10} \frac{1}{T} \quad (6-1)$$

from which it is easily seen that

$$A = abc \quad (6-2)$$

If we can measure absorbance, A , then quantitative analysis is reduced to maximum mathematical simplicity. Modern spectrometer charts for chemical use are now printed with an absorbance scale; instead of making the ordinate scale linear (transmission, or T), the ordinate scale is a non-linear one in units of the logarithm of the reciprocal of T , so that absorbance is measured directly. An absorbance and transmission scale are compared in Figure 6-8.

In order to perform a quantitative analysis it is necessary to determine the amount of absorbance increase that results only from light absorption by the molecule whose concentration we wish to determine. In the following

discussion it will be assumed that the material which is to be analyzed is the only one having an absorption band at the wavelength we have chosen to perform the analysis. This requires a little care in selection of the absorption band to be used. While it is still possible to perform quantitative analysis at wavelengths where more than one component has strong absorption, this is a relatively tedious process, and not usually suited to the philosophy of using "tabletop" spectrometers, that is, to obtaining results quickly. Chapter 2 in this book discusses this problem and gives references to more extensive treatments on the subject.

Even when an absorption band to be used in analysis is free from interference by bands of other compounds, determining its absorbance is not always easy, for the total amount of light attenuation at the analytical wavelength results from several additional causes: reflection at cell window faces, solvent absorption, scattering by nonuniformities in cell windows and the solution, electronic absorption, and nonspecific absorption by all the components in the mixture. Because these effects are small, and, most particularly, because they do not vary rapidly as a function of wavelength, corrections for them can be made by the use of the so-called "base-line" technique. The base-line, which corrects for light attenuation from causes other than absorption by the component of the sample to be measured, is established by asking the question: how would the spectrum appear if this absorption were not present? In Figure 6-8 is shown a portion of what might

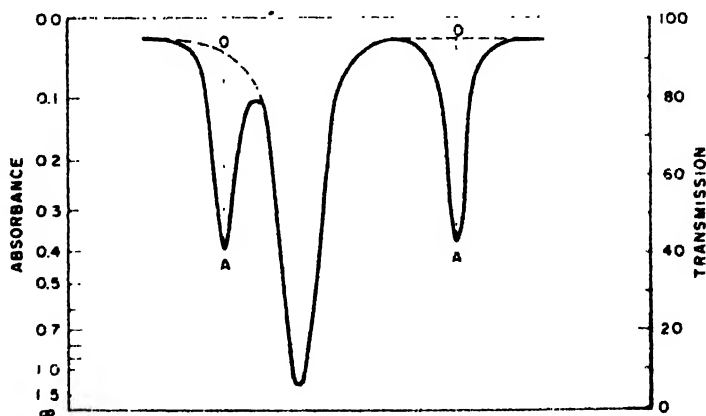


FIGURE 6-8. Base-line technique.

be a typical spectrum; clearly, the dashed line will be a very close approximation to what the spectrum would probably be if the component having the absorption bands were not present.

From this base-line the net absorbance of the band is easily determined; the ordinate value on the absorbance scale of point A is read, and from this number is subtracted the ordinate value on the absorbance scale of point O. This net absorbance is directly proportional to the concentration of the material causing the absorption band, and in order to determine its concentration it is necessary only to compare it with a number similarly obtained under conditions where the concentration is accurately known (i.e., a "standard" spectrum).

In some cases the base-line is not so easily determined, particularly if the spectrum is complex and consists of many bands. The base-line can only be reliably established to the extent that the question, "how would the spectrum appear if this absorption band were not present" can be answered. If it is possible to obtain a material which is identical in composition to the one containing the component to be determined, but without this component, then the base-line can be unequivocally established by simply obtaining the spectrum of such material. In some cases this is possible (all other components of the mixture are known or can be determined). But in materials resulting from new syntheses, or syntheses known to produce components of indefinite composition, this is not possible. Unfortunately, it is these latter cases that the organic chemist must deal with most often, and to the extent that the base-line is uncertain, the concentration of the component to be measured is uncertain. The situation is not hopeless, however, for inspection of the absorbance scale of Figure 6-8 shows that in regions of high transmission the absorbance scale is least sensitive to transmission uncertainty. Therefore, even though a base-line cannot be located with high precision, the error made thereby will not be too large provided the band to be measured has a relatively high absorbance value (i.e., is a relatively strong band).

It has been shown¹⁵ that highest precision results when the band being used for quantitative analysis is in the range 25 to 50% transmission (absorbance of 0.3 to 0.6). Bands much weaker than this give too little sensitivity, while bands much stronger than this are too sensitive to noise level uncertainty and errors in the 0% transmission point. For bands in the absorbance range 0.3 to 0.6 for which the base-line can be accurately determined, the analytical precision to be expected is of the order of $\pm 3\%$ of amount present.* This precision can be increased somewhat by obtaining the spectra of unknown and standard sequentially and repetitiously. However, the rapid determination of yield to $\pm 3\%$ is usually sufficient for most organic research; if higher precision analysis is desired, either other methods should be used, or, if infrared methods are to be used, it is sug-

*This is approximately the precision that will result with "tabletop" spectrometers when the standard slit program is used.

gested that more sophisticated instrumentation and techniques be employed.

In cases of purity determination (of solvents, starting materials, purified product), $\pm 3\%$ is perhaps not tolerable. In most cases it is better practice to determine the impurities specifically (e.g., $5 \pm 0.1\%$ of benzene in toluene) rather than to rely on assay as an index of purity (e.g., $95 \pm 3\%$ toluene). If the specific impurities have strong, unique bands in regions where the major component has little or no absorption this is easily accomplished by using thicker absorption cells or higher concentrations.

Some specific examples of the quantitative applications of infrared spectroscopy to organic research are given in the following section.

Following a Reaction

Determination of Conversion and Yield. Quantitative infrared analysis is an effective tool for following the course of many chemical reactions. Employing the methods described above, crude reaction mixtures often can be analyzed for starting materials and products to obtain yield and conversion data without actually physically separating and measuring the various components. The time saved in eliminating unnecessary distillations and crystallizations in reaction work-ups is considerable. Furthermore, due to material losses during these isolation processes, particularly when carried out on a small scale, yields and conversions based on infrared examination of crude reaction mixtures may actually be more accurate.

This application is particularly useful in process development where essentially the same reaction is carried out repeatedly with varying catalysts, reactant ratios, solvents, temperatures and pressures. Such an on-the-spot examination of the crude reaction mixture may give immediately the information necessary to alter process conditions as the experiment progresses. By judicious use of this technique it is possible in many cases to maximize yields with a minimum number of experiments.

Kinetic Studies. Infrared spectrometry has been used to determine the speed as well as the course of chemical reactions. In a series of papers entitled "Kinetics of Three-compound Equilibrations" by R. H. Allen and co-workers,^{1a,b,c,d} studies of isomerizations of aromatic hydrocarbons are described. Thus, in a typical case^{1c} the reaction vessel is charged with toluene (solvent), aluminum chloride (isomerization catalyst) and *o*-ethyltoluene (reactant). At specific time intervals, 25 ml portions are withdrawn, washed, dried, and scanned by infrared to determine the distribution of the resulting *ortho*-, *meta*-, and *para*-ethyltoluenes.

In their study of the isomerization of xylenes,^{1b} these workers used vapor phase chromatography as an auxiliary tool to separate and analyze for *o*-xylene because the toluene employed as solvent interferes with the infrared measurement of small amounts of *o*-xylene. This illustrates the complemen-

tary nature of infrared and vapor phase chromatographic techniques. Each tool extends the accuracy and usefulness of the other. The newer preparative vapor phase chromatographic columns may often be used advantageously to prepare pure samples for infrared standards.

Infrared has been found useful in kinetic studies where apparently simple chemical methods are subject to error due to interferences caused by other reactants or products. Thus, Meguerian and Clapp¹³ found that the conventional iodine method for mercaptans gave erratic results when applied to their rate studies of the reaction of benzenethiol with ethylenimines. Interferences apparently were due to starting ethylenimine in addition to the aminoethyl sulfide product. By use of the infrared method, measuring the relatively weak sulfhydryl band at 3.88μ (2575 cm^{-1}), they were able to study the reaction kinetics. This publication describes in detail the application of the base-line technique to their problem.

In order to follow very fast reactions by infrared spectrometry, it is necessary to modify the scanning mechanism so that the spectrum can be swept across the detector several times per second. Such modified instruments with cathode ray oscillograph recorders have been described.⁵

Product Purity. Once a product is isolated, its purity may be established by comparing its infrared spectrum with that of a standard. Such an assay is commonly employed in purity specifications. An infrared specification is so meaningful, in fact, that some producers of organic chemicals are now supplying infrared spectra of their materials with each shipment. Contamination with by-products or solvents can then be readily observed. Some industrial customers now purchase materials to infrared specifications.

Intermolecular and Intramolecular Interactions. The organic chemist has used infrared spectroscopy both qualitatively and quantitatively, to determine the existence and degree of intermolecular and intramolecular interactions.

Hydrogen bonding. Hydrogen bonding in phenols, alcohols, mercaptans, amines and oximes has been widely studied by the infrared method. Infrared spectroscopy provides a convenient tool for studying the effects of temperature, concentration, solvent, and pressure on hydrogen bonding in addition to facilitating the correlation of hydrogen bonding with physical and chemical properties. An entire chapter in a recent book on the hydrogen bond by Pimentel and McClellan¹⁴ is devoted to applications of infrared and Raman techniques. The closely related subject of chelate complexes has likewise been of considerable recent interest to the organic chemist. Thus, in a typical case, Belford² explains some of the molecular properties of the Cu (II) bisacetylacetonate coordination complex with the assistance of spectroscopy.

Association of acids. The nature and degree of association of acids has a definite influence on their chemical and physical properties. This association may be determined by spectroscopic means. In a study by Wilmshurst,¹⁷ it

was shown that acetic acid is nearly completely monomeric in the vapor state at 150°C and essentially dimeric at 25°C. At 65° and 105°C it exists in a dimer/monomer ratio of approximately 2:1 and 1:2, respectively.

Intramolecular complexes. Infrared has been used to detect the existence of and even to prove the structure of intramolecular complexes. The molecular addition compound of iodine and dimethylacetamide¹⁶ appeared to involve coordination through the carbonyl oxygen rather than through the amide nitrogen. This was indicated by the shifting of the carbonyl band to a frequency 43 cm^{-1} lower whereas no change was detected in the C-N frequency as compared with dimethylacetamide itself.

Following Separation Processes

Infrared spectroscopy offers a convenient and rapid control method for guiding a variety of separation processes. It not only gives an indication of whether or not a separation has been achieved, but it may make possible the identification and quantitative estimation of the various components.

Extraction. Infrared examination of extracts may show which components are being extracted. Likewise examination of succeeding extracts will determine when the extraction is complete, thus indicating the efficiency of the extraction process. When used in connection with extractions it is often convenient to use carbon tetrachloride as the extraction solvent instead of the more conventional ether or benzene. By using carbon tetrachloride the extract is immediately ready for infrared examination. Furthermore, the flammability and explosive hazards of ether are avoided.

Distillation. The routine examination of each distillation cut is highly recommended. In this manner the efficiency of the distillation can be followed as the distillation progresses making possible immediate changes in reflux ratios as dictated by the results obtained. In addition, spectra of by-products will be available for identification.

Recrystallization. Infrared analysis has been used advantageously to determine the efficacy of recrystallization procedures. This gives the chemist a check, not only on the possible by-products present as impurities, but also on the presence of recrystallization solvent. The occasional¹ formation of hydrates or alcoholates during recrystallization can also be detected.

Chromatographic Separation. The combination of infrared spectroscopy and vapor phase chromatography has already been mentioned briefly. These tools are an extremely powerful combination. Infrared can usually determine the degree of separation achieved by the gas chromatograph. Collection of VPC cuts and subsequent infrared examination is a much more reliable identification method than effluent times. Isolation of impurities using the gas chromatograph, and collection and identification by infrared micro-techniques should be employed routinely by the organic researcher. In the

order of one microliter of sample is required for a satisfactory spectrum using the technique described by Grasselli and Snively¹⁰ or by the very simple capillary collection system described by Lohr and Kaier.¹¹

Perhaps the ultimate in following separation processes is presented by the work of Bellamy³ and Goulden.⁹ Quantitative and qualitative evaluations of paper chromatograms were carried out by infrared using thin paper (e.g., Whatman No. 50) and differential analysis with paper in the reference beam. Various aromatic nitro compounds and amino acids were identified and quantitatively estimated.

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CHAPTER

7

Pharmaceutical Applications of Infrared Spectroscopy

James L. Johnson, Robert W. Rinehart
and C. Leroy Graham**

INTRODUCTION

Infrared spectra are valuable in pharmaceutical research, development, and quality control because of their usefulness in: (1) qualitative analysis, (2) quantitative analysis, and (3) identification. The purpose of this review is to describe uses which are more or less unique to the pharmaceutical field, and to summarize key parts of the pharmaceutically-oriented literature. This, by definition, includes work on drugs in the pure state and in formulations employed in the practice of medicine, related compounds of biological origin, and complex systems such as microorganisms or animal tissues which may be affected by drugs. A further delineation of the scope of this review is embodied in the definition of a drug as a compound or noninfectious biological substance used in medicine because of some physiological activity.

A complete literature survey is not an objective in this work. Virtually no mention is made, for example, of the numerous theoretical papers which will have great importance in applied infrared spectroscopy in the future.

The pharmaceutical industry uses central infrared laboratories extensively, but more and more organizations are gaining wider usage for qualitative studies by placing instruments in all areas concerned with organic chemicals. Instruments in such locations yield ready answers to such questions as the selectivity of a reaction, the success of a purification step,

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the completeness of a derivative-forming reaction, or the identity of a gaseous by-product. The central laboratories, in these decentralized situations, are usually responsible for the special techniques and equipment needed for less frequently met problems requiring, say, elaborate gas handling and microsampling. This review will give leads into literature important to both primary and supportive infrared programs.

Infrared spectra for identification purposes are of particular interest in the pharmaceutical field. They have gained industry-wide acceptance and legal status. Infrared identity tests were used in the Sixteenth Revision of "The Pharmacopeia of the United States" and the Eleventh Edition of the "National Formulary." Infrared spectra have come to be accepted characteristics for inclusion in patent applications covering antibiotics of unknown structure and in new drug applications. These uses are unique to the pharmaceutical industry.

Quantitative infrared analyses meet needs arising with research and development studies, pharmacy research, chemical production, and pharmaceutical production. In research and pilot areas, the data aid in studying reaction conditions and yields, and in measuring the purities of intermediates. In pharmacy research infrared analyses provide essential answers to such questions as the stability of a drug in its supporting or protecting matrix. The use of infrared methods for quality control serves chemical production needs relating to bulk drugs, and pharmaceutical production needs with finished pharmaceutical forms. It is interesting that the industry as a whole uses batch processes in chemical production so that its applications of continuous analysis are at a minimum, and are mainly restricted to research studies.

TECHNIQUES

In pharmaceutical work certain variations on the basic techniques described in Chapter 2 serve three needs characteristic of research on natural products. In this special sense the study of a drug or its metabolite in a biological system is regarded to be a natural product problem. The first need is for conserving precious and difficult-to-obtain material, the second is for some degree of quantitation in the absence of a standard sample, and the third is for handling numerous polar samples with unfavorable solubility properties. Aqueous solutions are of special interest in this last area.

The problems encountered in handling polar samples and samples soluble only with difficulty have stimulated the development of techniques such as mulling, the potassium bromide pellet, aqueous solution, stabilized suspensions and resolidified melts. Although many industries have contributed

in their development, the techniques have proven to be especially valuable in pharmaceutical work. The mull technique is probably the one most widely used. It is simple, easy, requires but little sample, and produces a minimum of changes in the sample. The potassium bromide technique^{117,118,125} is also widely used. Three procedures can be employed for mixing the sample with the powdered support, mechanical grinding, freeze drying, and deposition from a solution in a volatile solvent. The latter two procedures are preferred for small samples. They also offer the practical advantage of fewer difficulties in interpreting the data because of general absence of spectral variations resulting from polymorphism and decomposition.¹¹⁰ Relatively simple techniques for making small pellets permit the study of samples as small as 15 micrograms in conventional spectrometers.^{56,76} More demanding procedures which yield spectra with one microgram of sample, or even less, are available. These require micro-dies and beam condensers.

The practice of preparing mulls directly on salt plates is especially noteworthy as a means of conserving material. A one-milligram sample can yield complete data in the 4000 to 650 cm^{-1} region. The carbon-hydrogen regions may be examined using hexachlorobutadiene as a mulling agent.⁴ The mull may then be opened up by pulling the supporting salt plates apart, and the volatile hexachlorobutadiene allowed to evaporate. Mineral oil can then be added, and a new mull prepared for study in regions obscured by the absorption bands of hexachlorobutadiene, (Figure 7-1). Potassium bromide pellets^{117,118,125} provide the most convenient means of handling samples in the 1 to 100 microgram range. Techniques and small cells for solution work in this range of sample sizes have also been described.³¹ Purified samples amounting to about 100 micrograms can be obtained using gas, column, or thin layer chromatography, so that combinations of these techniques with infrared become powerful tools.

The matter of achieving some degree of quantitation in the absence of a pure standard sample is typified by the early work of Barnes, Gore, Williams, Linsley, and Petersen⁷ on the infrared assay of penicillins. Crude samples could be analyzed satisfactorily only after a positive correlation was established between the strength of the 1770 cm^{-1} absorption band of the various penicillins and their biological activities. This approach is possibly easier to apply in the pharmaceutical field than in other chemical areas because of the relatively easy access to biological assays. It is often possible, however, to assume the strength of a given band as indicating the relative concentration of a desired component, and to validate the infrared assay by isolating the component.

Aqueous solutions offer increasing interest and promise in pharmaceutical research because most drugs serve their intended purposes in essentially

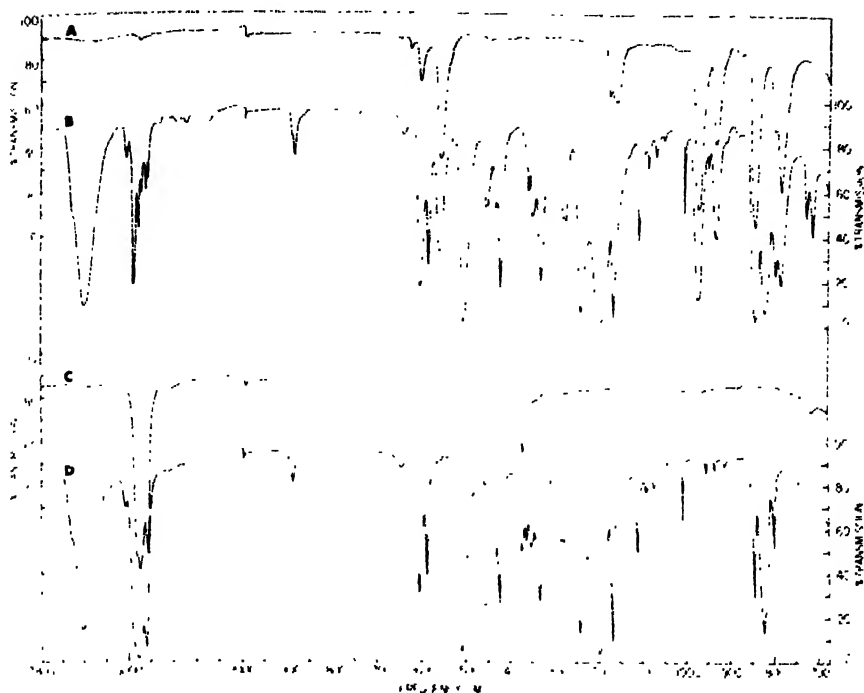


FIGURE 7-1.

- (A) Hexachlorobutadiene.
 (B) Diethylstilbestrol mulled with hexachlorobutadiene
 (C) Mineral oil.
 (D) Diethylstilbestrol mulled with mineral oil.

aqueous systems. The potential of infrared measurements for observing drugs at work has not been fully exploited, but the literature does contain stimulating leads in the form of reports on successful work in water solutions with small molecules such as alcohols, fatty acids and their salts and amino acids.^{49,92,105} Blout^{13,14} Lenormant⁸² and Goulden⁵¹ described applications involving complex molecules such as proteins, nucleic acids, and polypeptides, and extended their observations to include the effects of pH changes on some of the systems. Wood¹⁴⁴ examined single muscle cells, and observed that the spectra resembled those of the major protein components, myosin and actomyosin, but showed differences for different muscles from the same animal, and for the same muscle from different species. Kaye⁷² and Sternglanz¹²² investigated the optical window materials available for use with water prior to 1960. Their studies included glass, quartz, sapphire, lithium fluoride, calcium fluoride, arsenic trisulfide, barium

fluoride, germanium, silver chloride, and thallium bromide-iodide. Gore, Barnes, and Petersen,⁴⁹ and Blout and Lenormant¹² illustrated the use of deuterium oxide to bring out spectral information obscured by water. The announcement of Irtran-2³⁹ as a new water-resistant window material has been a further stimulus to work with aqueous systems.

The attenuated total reflectance (ATR) technique²¹ is a practical infrared method for qualitative and quantitative analyses using aqueous solutions.⁷¹ The short effective path length used in this method is responsible for both its major advantage and disadvantage. The advantage is that good spectra may be obtained in all parts of the rock salt region except the vicinity of the 3300 cm^{-1} water band. The disadvantage is that highly concentrated solutions, usually 20% or greater, are required.

Resolidified melts, a classic technique, have recently been revived for studying polymorphism and solvation.⁵¹ This technique proved especially valuable in working with insoluble compounds, and with substances whose significant bands fall under interfering solvent absorptions. Decomposition at the melting point gave little difficulty. Insoluble materials have also been prepared as suspensions in organic solvents using aluminum stearate as a stabilizer. This technique has been reported to be adequate even for quantitative work.³⁷

The demands for standardized instrument performance resulting from the industry-wide acceptance of U.S.P. XVI, and N.F. XI, infrared identification tests raised interesting problems. The needs are currently being met with standard reference samples, but increased attention is being focused on wider use of the calibration procedures pioneered by Oetjen, Kao, and Randall⁹⁸ and expanded in later reports. These workers used 150 points in the spectra of NH_3 , CO_2 , and H_2O measured with a grating instrument which had been adjusted to a lesser resolution than usual in order to approximate that of a prism spectrometer. Plyler has defined check points in the spectrum of polystyrene to provide a system which is much easier to use on a day-to-day basis.¹⁰⁴ Jones⁷⁰ proposed an indene-camphor system which affords a greater number of check points than polystyrene. These systems are satisfactory for wavelengths, but the problem of absorbance stands unsolved.

THE SPECTROSCOPISTS' REFERENCE LIBRARY

The spectrum of an unknown sample presents a real and potentially very great challenge to the infrared spectroscopist. The interpretation may result in a simple identification, or it may require all of the experience and ingenuity which the spectroscopist can muster. An identification may

indicate that starting material was recovered from an attempted reaction, or it may show that a newly isolated natural product is a known compound. Prompt adjustments in a scientific program can be made in either case.

The spectra which do not result in identifications call for special attention. In the pharmaceutical field there are no limits on the types of structures which may be encountered, and the spectroscopist is very dependent on his collection of reference information; it cannot be too varied.

General References

The classic books on infrared spectroscopy are so well established that the need here is simply to mention the authors' names: Bellamy,⁸ Barnes, Gore, Liddel, and Williams,⁶ Jones and Sandorfy,⁶⁹ Randall, Fowler, Fuson, and Dangel,¹⁰⁸ Hershenson,⁵⁷ Szymanski,¹²⁷ Herzberg,^{58,59} and Wilson, Decius, and Cross.¹⁴³

Sunshine and Gerber¹²⁶ included an atlas of spectra for 268 commonly used drugs as part of their book describing solvent extraction procedures for isolating identifiable amounts of drugs from blood. These spectra constitute a valuable reference compilation for certain drug identification problems.

A search of the periodicals often begins with the series of reviews prepared by R. C. Gore, and published in *Analytical Chemistry* beginning in 1959. This journal also collaborated with The Coblenz Society to initiate publication of the very useful series on Infrared Quantitative Analysis in October, 1957. This series appeared in *Analytical Chemistry* through December, 1960, and has been continued in *Applied Spectroscopy* since early 1961. A partial bibliography of biochemicals' spectra prepared by Clark and Chianta²⁹ is of particular value in the pharmaceutical field. W. Kaye⁷²⁻⁷³ has prepared valuable bibliographies and reviews on work in the near infrared. A similar treatment has been accorded the far infrared regions by Bentley, Walforth, Srp, and Powell^{9,10-106} and by Palik.⁹⁹ These publications will undoubtedly have increasing value in future pharmaceutical work.

Chemical Abstracts is to be commended for the practice, begun in 1958, of subdividing the entries in the Spectra section so that references to infrared data are differentiated from those covering ultraviolet, visible, Raman, and x-ray data. This plan greatly facilitates surveying the more recent literature.

Spectral data coded into I.B.M. and McBee Keysort card formats are commercially available. These sets allow relatively inexpensive expansion of any laboratory's data library. The sources include the American Society for Testing and Materials,³ The National Research Council,⁹³ and Butterworths Scientific Publications.³⁶

Spectra collections including data for many compounds of direct and indirect pharmaceutical interest are also available from The American Petroleum Institute,² Samuel P. Sadtler and Sons, Inc.,¹¹⁴ and The Manufacturing Chemists Association.⁸⁷

Steroids

The steroids comprise the most thoroughly documented group of compounds encountered in the pharmaceutical field. This is due in large part to the work of R. N. Jones, K. Dobriner, and their associates at The National Research Council of Canada and The Sloan-Kettering Institute for Cancer Research. Steroids are exemplary compounds for qualitative infrared work because the relatively rigid perhydrophenanthrene nucleus serves to restrict the ranges for group absorptions. A two-volume atlas^{15,111} contains spectra for about 650 steroids, and Volume II includes a valuable discussion section which facilitates interpretive use of the spectra. This discussion includes an impressively complete tabulation of structure-spectra correlations containing more than 450 entries, and keyed to a bibliography listing the original publications. A review by Jones and Herling⁶⁸ also contains a majority of this bibliographic information. Other reviews such as those by Rosenkrantz¹¹² and Cole³² contribute different perspectives on the vast steroid literature.

Absorption intensities for carbonyl bands in steroid spectra⁶⁷ have proved to be especially useful. Again the relatively rigid perhydrophenanthrene nucleus contributes to constancy so that groups absorbing at the same frequencies, but having different absorptivities, can be differentiated.

Barbiturates

The commercially important barbiturates typify one extreme aspect of pharmaceutical infrared. These compounds, as a group, are the organic poisons most often encountered at autopsy in medico-legal situations. Their spectra as mulls,^{18,84} KBr disks,^{30,86} and chloroform solutions,¹²⁹ have been compiled as identification aids. Levi and Hubley⁸⁴ also found the spectra of barbiturate-copper-pyridine complexes to be useful for identification, and to complement the spectra of the free acids.

Alkaloids

Alkaloids have also received attention from the forensic^{61,83,103} and research^{88,94} points of view. Spectra for more than 100 alkaloids have been published.

Carbonyl Compounds

The broad types of carbonyl compounds are adequately classified in the works of Bellamy,⁸ and Jones and Sandorfy.⁶⁹ Nevertheless, the identifica-

tion of a specific compound is often aided by collections of data on homologous series such as the sodium salts of fatty acids,²⁸ the 2, 4-dinitrophenylhydrazones,^{65,113} or dimethylhydrazones¹⁴² of groups of aldehydes and ketones.

Lipids

Infrared data have a great many applications in working with fatty acids and related substances, both natural and synthetic. Some 100 band assignments have been recorded for structural moieties of interest in studying *cis-trans* isomerism,⁹⁶ degree of unsaturation,¹⁴⁰ polymorphism of glycerides,^{26,119} chain length,⁶⁶ chain branching in the sodium chloride⁴² and lithium fluoride⁵⁴ prism regions, lipoproteins,⁴³ and metal soaps.^{28,55} Near infrared spectra of fatty acids have value in virtually all of these problems.⁶⁰ Demanding quantitative problems such as purity determinations can often be handled by the differential analysis technique²⁹ or by use of integrated intensities.¹⁴⁰ Freeman⁴⁴ has extended the work to a study of serum lipids with the view that blood samples, which are readily available in a clinical laboratory, might yield additional diagnostic information.

Amino Acids and Proteins

Amino acids have been studied in potassium bromide pellets,^{75,81} and in aqueous solutions in different pH ranges.³⁸ Spectra for dinitrophenyl⁴⁵ and thiohydantoin¹⁰⁷ derivatives of amino acids have proved useful in identifying N-terminal groups in peptides and proteins. In fact, descriptive data for the polymers themselves have come from infrared studies.^{1, 14, 15, 16, 82} In related studies ribonucleic and deoxyribonucleic acids have been shown to have characteristic infrared spectra.¹¹

Bacteria

Phages and bacteria have been studied to gain spectral support in their taxonomy. Six serologically different phages showed the absorption bands of ribonucleic and deoxyribonucleic acids, but could not be unequivocally distinguished.⁷⁸ More positive results have come from the study of bacteria; genera are quite easily distinguished. Species can often be characterized, but the method fails with strains which often exhibit spectral differences approaching the magnitude of errors in the technique.^{52, 79, 109, 123} Additional resolution in the identification of bacteria has come from studies on the lipids which may be extracted from them.^{97, 140}

Inorganic Compounds and Gases

Collections of data on 159 inorganic compounds⁹⁰ and 64 minerals⁶² provide important reference material for approaching any analysis of tablet excipients. A bibliography of references to spectra of inorganic sub-

stances appearing in *Chemical Abstracts* in the 1952 to 1958 period is a valuable complement to these collections.⁸⁰

Clinical Applications

The detection of drugs and metabolites in clinical research offers a challenging opportunity to infrared spectroscopists. The barbiturates encountered in medico-legal situations are representative of more difficult cases which have been handled successfully. Infrared microtechniques are especially applicable in this area.

The work of the Dow group on the anesthetic, methoxyflurane, should serve to illustrate the extent to which infrared can be used to study a compound from the clinical standpoint. A carbon disulfide extraction step, first used by Stewart and his associates,¹²⁴ was modified to allow precise measurements of levels of the anesthetic in arterial and venous blood during a 90-min anesthesia.²⁷ Runs were accomplished on 2-cc samples of blood. Infrared was also used to monitor the concentration of anesthetic in inspired air³⁹ with the net result being a rather complete picture of the anesthetic concentration at key stages in the anesthesia.

The implications for clinical usage of infrared become apparent when viewed against this background. Great strength can derive from infrared spectra as a means of identifying a material even when other methods serve better as a means of analysis.

The extraction procedures and atlas of spectra published by Sunshine and Gerber give strong support for this type of work.¹²⁶

QUALITY CONTROL

Industry-Wide Quality Control: Infrared Tests in the Official Compendia of The United States

Infrared tests have industry-wide and legal status only in the pharmaceutical industry where the function of the Quality Control Laboratory is so vital. This unique industry-wide use of infrared tests began when the Sixteenth Revision of "The Pharmacopeia of The United States" and the Eleventh Revision of "The National Formulary" became official on October 1, 1960. U.S.P. XVI used 89 infrared identification tests for 52 organic medicinals in bulk and in various dosage forms. N.F. XI used six such tests for five drugs. U.S.P. XVI also used two quantitative infrared assays. The magnitude of the accomplishment may be emphasized by giving recognition to the fact that no infrared tests were used in U.S.P. XV or N.F. X which became official in 1955.

The infrared identification test supplements traditional criteria of identity such as color reactions, melting point, ultraviolet spectrum, refractive index, and optical activity which often leave greater doubt regarding the identity of a sample than does an infrared spectrum. This extensive use of infrared identity tests in these compendia, considering the cost of the instruments and the technical problems involved in their utilization, shows the value placed upon them.

When work on U.S.P. XVI and N.F. XI began, it was found that infrared techniques were so well established in the laboratories of state and national regulatory agencies, universities, and in the manufacture and control of pharmaceuticals that the inclusion of infrared tests in the compendia was assured. This inclusion was facilitated by the key works of Carol,²⁴ Canback,¹⁵ and Gennaro and Osol,⁴⁸ and by the trial publication of infrared spectra for some sixty medicinal agents in *Drug Standards*, January 1957 to August 1959, by The Chemical Laboratory of The American Medical Association, under the direction of Walter Wolman.

The decision to include infrared tests in U.S.P. XVI and N.F. XI required further decisions regarding the best format for presenting the tests. Reference standards for preparing comparison spectra were specified in all but one of the tests in the compendia. This choice makes the identification essentially independent of instrumental and procedural variations since the standard and unknown spectra are prepared under the same conditions. The other techniques considered were: (1) including the spectrum of a high purity sample of the drug in the monograph, and (2) listing the wavelengths and intensities of the bands observed for high purity samples of the drugs.

The U.S.P. XVI specified the potassium bromide disk for 54 tests, petrolatum mulls for 8, and carbon disulfide solutions for 28. The following tests illustrate the formats employed for KBr disk and mull spectra in U.S.P. XVI, Figures 7-2 and 7-3.

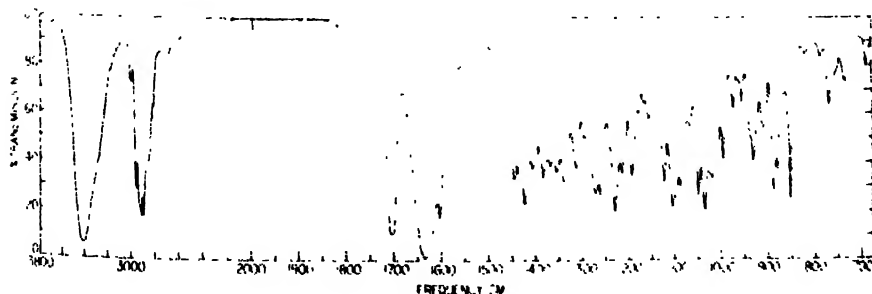


FIGURE 7-2. Hydrocortisone in KBr disk.

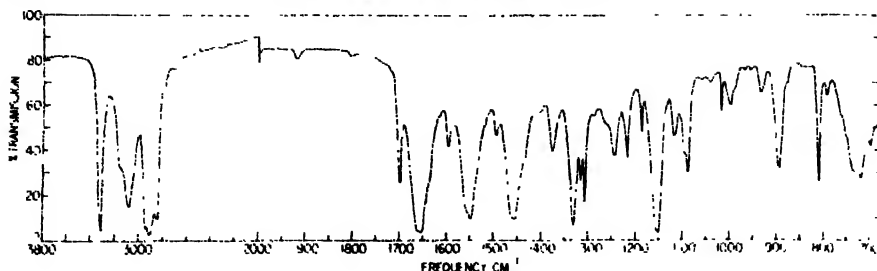


FIGURE 7-3. Tolbutamide in mineral oil mull.

Hydrocortisone Identification Test — “The infrared absorption spectrum of a potassium bromide dispersion of Hydrocortisone, previously dried at 105° for 3 hr., exhibits maxima only at the same wave lengths as that of a similar preparation of U.S.P. Hydrocortisone Reference Standard. If a difference appears, dissolve portions of both the sample and the Reference Standard in a suitable solvent, evaporate the solutions to dryness, and repeat the test on the residues.”*

Tolbutamide Identification Test — “The infrared absorption spectrum of a liquid petrolatum dispersion of Tolbutamide, in the range of 2 to 12 μ , exhibits maxima only at the same wave lengths as that of a similar preparation of U.S.P. Tolbutamide Reference Standard.”*

The tests requiring petrolatum mulls are in the minority but at present there is a shift toward more widespread use of mulls as sample mounts. This technique is generally agreed to be easier to use and to give less difficulty with polymorphism, frequency shifts, and variations in band intensities than potassium bromide disks.¹⁰

Carbon disulfide solution spectra are a part of the requirements of the following general procedure for the identification of organic nitrogenous bases.

“Identification — Organic Nitrogenous Bases. — Dissolve 50 mg. of the organic nitrogenous base, if in bulk, in 25 ml. of water, or shake a quantity of powdered tablets or the contents of capsules equivalent to 50 mg. of the salt with 25 ml. of 0.01*N* hydrochloric acid for 10 minutes. Transfer the liquid to a separator, if necessary filtering it and washing the filter and the residue with several small portions of water. In a second separator dissolve 50 mg. of the corresponding U.S.P. Reference Standard in 25 ml. of water. Treat each solution as follows: Add 2 ml. of sodium hydroxide T.S. and 4 ml. of carbon disulfide, and shake for 2 minutes. Centrifuge if necessary to clarify the lower phase, and filter it through a dry filter, collecting the filtrate in a small flask provided with a glass stopper. Determine the absorption spectrum of the filtrate in a 1.0 mm. cell between 7 μ and 15 μ , with a suitable infrared spectrophotometer, using carbon disulfide in a matched cell as the blank. The spectrum of the solution prepared from the sample shows all of the significant absorption bands present in the spectrum of the solution prepared from the Reference Standard. If the spectrum of the sample preparation possesses obscuring absorption bands not present in that of the standard preparation, the sample may be further purified.”*

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To date, little use has been made of quantitative infrared procedures in either of the official compendia. Two such tests appeared in U.S.P. XVI. The test for Acetazolamide is illustrative, Figure 7-4.

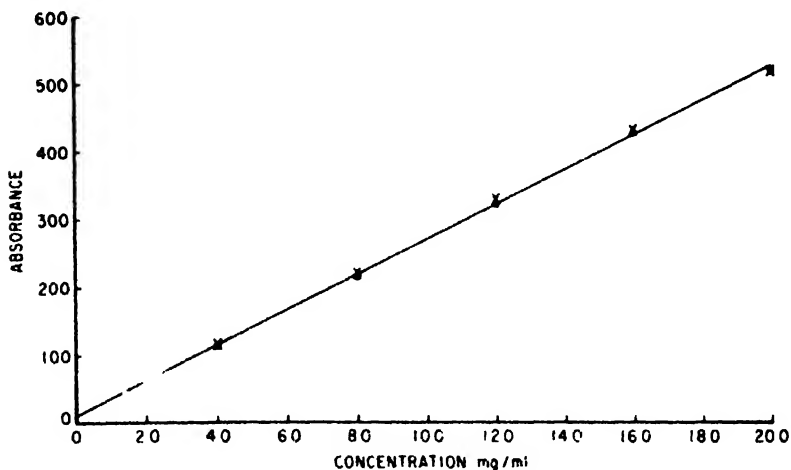


FIGURE 7-4. Absorbance vs concentration plot for acetazolamide in pyridine solution: wavelength, 7.38μ , cell thickness, *ca.* 0.1 mm.

"*Assay.*"—Dissolve about 200 mg. of Acetazolamide, accurately weighed, in a small volume of pyridine in a 10-ml. volumetric flask, add the solvent to volume, and mix. Determine the absorbance of this solution in a 0.1-mm. cell at 7.38μ , with a suitable infrared spectrophotometer. Calculate the quantity, in mg. of $C_4H_6N_4O_3S_2$ in the portion of Acetazolamide taken by the formula $10,000(A/a)$ in which A is the absorbance of the solution and a is the absorptivity of U.S.P. Acetazolamide Reference Standard, determined similarly in a solution in pyridine containing about 20 mg. in each ml."

The somewhat general reluctance to establish official quantitative infrared tests has originated with concern about the problems of standardizing such methods. This hesitancy is disappearing rapidly. A research application of quantitative techniques to the three-component system, aspirin anhydride, aspirin, and salicylic acid involved standard errors of 0.9%, 0.4%, and 0.2%, respectively.⁴⁷ This study shows the order of precision to be expected from this type of assay.

Intracompany Quality Control

Tests comparable to the above examples serve many pharmaceutical companies as operating or internal controls for an ever-increasing number of bulk drugs, intermediates, and chemical raw materials. The success of these newer methods has been striking, and assures the use of additional infrared-based specifications in future revisions of the U.S.P. and N.F.

Bulk Drugs. The assaying of bulk drugs is basically the simplest of the internal quality control applications of quantitative infrared spectroscopy. In general, substances soluble to the extent of 0.5% or more in suitable infrared-transparent solvents are amenable to infrared assays such as the one quoted above for acetazolamide. The U.S.P. XVI assay for diethyltoluamide specifies carbon disulfide as the solvent. Washburn^{134,138} used chloroform solutions for analyzing erythromycin and mixtures of chlorcyclizine and pramoxine. Coy, Sabo, and Washburn³¹ also employed chloroform in assaying procaine penicillin G.

Samples not sufficiently soluble in suitable solvents can often be handled by converting the materials to derivatives which are soluble. Wright¹⁴⁵ isolated free penicillin O acid from the potassium and 2-chloroprocaine salts of penicillin O and measured this acid in chloroform. Carol, Molitor, and Haenni,²⁰ and Nachod, Henkel, and Fippin⁹ converted estrone, equilin, and equilinen to benzenesulfonates and gained sufficient carbon disulfide solubility for analysis. Carol later employed the same procedure for estradiol-17 β .²¹

Assays in the solid state have been used when solutions were not feasible. Barnes and co-workers⁷ and Garlock and Grove⁴⁶ assayed penicillin G salts in liquid petrolatum mulls. Barnes and his associates used D, L-alanine as an internal standard, and Garlock and Grove employed a spacer cell to assure a fixed path length. The potassium bromide pellet technique has also been used for quantitative work with sparingly soluble compounds. Carol²⁵ employed the technique for ethinyl testosterone and Jensen⁶³ used it for sodium penicillin G. Dolinsky³⁷ used aluminum stearate stabilized suspensions in carbon tetrachloride or carbon disulfide to analyze mixtures of sulfamethazine with sulfamerazine, and F. D. and C. Orange No. 1 with D. and C. Orange No. 4.

Pharmaceutical Formulations. In contrast to the situation with bulk drugs, the assaying of pharmaceutical formulations represents the most complex analytical area for drugs which have progressed beyond the research stages. Kennedy has prepared a succinct imagination-stimulating paper on this application.⁷⁴ Formulations which do not involve galenicals or biologicals present simpler problems by virtue of being prepared mixtures involving known components. Galenicals and biologicals, like research systems, often defy infrared assay, or involve such great amounts of developmental research that the infrared approach is impractical.

The nature and amounts of excipients in formulations vary widely. The success of infrared assays, therefore, depends on the availability of procedures for isolating the component of interest in relatively pure form.

Solvent extractions have been used widely. The general pattern has been to extract the drug with a solvent chosen for its affinity for the drug.

and to make the spectral measurements directly on the extract or to shift to an optimum infrared solvent by evaporating and redissolving. Papineau-Couture and Burley¹⁰⁰ analyzed pregnenalone acetate tablets using acetone for the extraction, and carbon disulfide for the spectral measurements. A direct carbon disulfide extraction served for atropine sulfate^{22 23} nitroglycerine, meperidine, codeine, and amidone.²² The following procedure for atropine sulfate is typical.²²

"Weigh a counted number of tablets and reduce to a fine powder without appreciable loss. Weigh accurately a portion of the powder equivalent to 10–12 mg. of atropine and transfer to a 125 ml. separator. Add 5 ml. of H₂O, mix thoroughly, and make distinctly alk. with dil. NH₄OH soln. Ext. with 4 successive 25 ml. portions of CS₂, filtering each thru a dry filter into a 150 ml. beaker. Carefully evap. the combined ext. to ca 3 ml. and transfer to a 5 ml. volumetric flask with the aid of small amounts of CS₂. Dil. to vol. and mix thoroughly. Carefully weigh 25 mg. of atropine, transfer to a 10 ml. volumetric flask, dissolve in CS₂, dil. to vol., and mix thoroughly. Det. the absorbance of the sample soln and standard soln relative to solvent blanks at 9.66 μ . Compare the recorded spectra of each soln from 2–15 μ in order to ascertain the identity of the sample.

$$\text{Atropine sulfate in sample} = \frac{A_{\text{sample}}}{A_{\text{standard}}} \times 2.5 \times 1.2^{**}$$

Schwartzman¹¹⁸ analyzed nitroglycerine preparations by a modification of this procedure wherein he utilized a base-line technique with a band at 7.90 μ . Washburn and Krueger¹³⁰ used direct readings on chloroform extracts, and a series of graphic approximations for multicomponent analyses on phenacetin, aspirin, and caffeine tablets. A modification of this procedure allowed the analysis of the same components with theerjirvamine, the latter being assayed as the reineckate.¹³¹ Further work showed that direct solution of all of the active components in chloroform could be used to assay the multicomponent formulation.¹⁰¹ In a combination of phenacetin, aspirin, caffeine, and codeine, the latter was determined by infrared following a carbon disulfide extraction.¹⁰¹

Aqueous suspensions of pregnenalone have been assayed by filtering out the solid steroid and dissolving the residue in carbon disulfide for analysis.¹⁰⁰

Washburn extended the use of infrared analyses to elixirs and ointments. The National Formulary preparation, Iron, Quinine and Strychnine Phosphates Elixir, presented a frequently encountered aspect of formulations. The concentration of quinine phosphate was 70 times that of strychnine phosphate and therefore both components could not be determined at a single dilution. In the assay procedures the alkaloid bases were extracted from the elixir with chloroform after appropriate pretreatment and pH adjustment. The extract, on evaporating to dryness, gave a residue which

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was redissolved in chloroform at two dilutions for the spectrophotometric measurements.¹³⁵ Additional ingenuity was brought to bear on the problem of analyzing N.F. Iron, Quinine, and Strychnine Elixir where the concentration ratio of quinine hydrochloride and strychnine sulfate was 46 : 1. In this case strychnine was measured by an infrared method, and quinine by a fluorometric method.¹³⁵ The detailed procedure for the Iron, Quinine, and Strychnine Phosphates Elixir is illustrative of the type of simple extractive separations which can be used for elixirs.

"Transfer 30 cc. of sample to a 250-cc. beaker and place on a steam bath for fifteen minutes, or until reduced to a volume of approximately 25 cc. Transfer quantitatively to a 250-cc. separatory funnel and add dilute metaphosphoric acid until solution is acid to Alkacid paper. Extract gently with four 25-cc. portions of chloroform and discard chloroform. Add 2*N* sodium hydroxide to aqueous portion until alkaline to Alkacid paper. Extract vigorously with four 15-cc. portions of chloroform, and combine chloroform extracts in a second 250-cc. separatory funnel. Wash with 10 cc. of 0.1*N* sodium hydroxide, and using a 25-cc. flask, evaporate to dryness under a stream of nitrogen. Dry for two hours in a vacuum desiccator.

"Dissolve residue in exactly 2 cc. of chloroform. Transfer 1 cc. of this solution to a small test tube, add 2 cc. of chloroform, and stopper tightly. Fill blank cell with chloroform and adjust slit for full scale deflection at 6.06μ . Fill the sample cell with concentrated solution prepared above and observe the optical density. With blank cell in place, adjust slit for full-scale deflection at 6.2μ . This operation should be done as rapidly as possible to prevent evaporation.

"The concentration of each component is computed by a two-component graphical calculation, allowing for the fact that the solution observed for the strychnine band at 6.06μ is three times as concentrated as that observed at 6.2μ for the quinine band."

Atropine Sulfate, 0.5% Ointment, required the multistep extraction procedure given below.¹³² Pilocarpine Hydrochloride, 2% Ointment, was analyzed by a similar procedure.¹³³ Scopolamine Hydrobromide, 0.2% Ointment¹¹⁸ and Phenacaine Hydrochloride, 1% Ointment¹³³ were determined by variations on the basic procedure¹³² in which 1*N* sodium hydroxide rather than ammonium hydroxide was used in making the aqueous phases basic.

"Transfer about 2 Gm. of ointment (accurately weighed) to a suitable flask. Dissolve in 15 cc. of ether and transfer to a separatory funnel. Rinse the flask with two 10-cc. portions of ether and transfer to the separatory funnel. Extract with five 10-cc. portions of water (rinsing each portion first through the original flask) and collect the aqueous phase in a second separatory funnel. Render the aqueous phase alkaline with 15% ammonium hydroxide. Extract with four 10-cc. portions of chloroform, collect the chloroform phase in a 50-cc. flask and evaporate it to dryness under a stream of nitrogen.

"Dissolve the residue by adding 5 cc. of 2% sulfuric acid and heat on a steam bath. Transfer the solution to a separatory funnel. Rinse the flask with three 10-cc. portions of 1% sulfuric acid, and add the rinsings to the separatory funnel. Wash the

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aqueous solution with one 20-cc. portion and three 10-cc. portions of chloroform. Render the aqueous phase alkaline with 15% ammonium hydroxide, and extract with four 10-cc. portions of chloroform. Filter the combined extracts through a chloroform-soaked pledget of cotton into a small flask, evaporate to dryness under a stream of nitrogen, and dry for one hour in a vacuum desiccator.

"Dissolve the residue in 2 cc. of carbon tetrachloride. (If the residue does not dissolve entirely in five minutes, apply gentle heating to the tightly stoppered flask.) Determine the optical density of the sample solution at 8.56μ in a sealed sodium chloride cell of 0.5 mm. thickness. Refer the observed optical density to the working curve and determine the concentration of the solution. Confirm the identity of atropine by running a qualitative curve on this solution from 8 to 9μ ."*

A study carried out by Banes⁵ on the assay of adrenal cortex extracts has provocative features for other formulations, biologicals, and galenicals. The extracts, which are mixtures of endocrine agents prepared from the adrenal glands of healthy domestic food animals, are assayed officially in terms of their capacity for promoting the deposition of liver glycogen in adrenalectomized animals.^{95,128} A predominant portion of this activity is attributable to four hormones: corticosterone, 11-dehydrocorticosterone, 17-hydroxycorticosterone, and 17-hydroxy-11-dehydrocorticosterone which, on a weight basis, have different potencies. Banes separated the four steroids by partition chromatography, monitored the fractions by infrared, and measured their concentrations by colorimetric techniques.

Process Intermediates. The analysis of process intermediates and chemical raw materials, as distinct from bulk drugs, has no feature which is unique to the pharmaceutical industry. The intended use of the materials in preparing drugs simply demands more critical and complete analyses because of the necessity for considering the biological activities of undesirable end-products. These end-products might result from impurities in raw materials or originate as by-products at intermediate process steps. Washburn has pioneered in this area too; he developed five of the six illustrative analyses listed in Table 7-1.

TABLE 7-1. ILLUSTRATIVE RAW MATERIAL AND INTERMEDIATE SYSTEMS

System	Reference
(1) Diethyldiethylmalonate in diethylethylmalonate	136
(2) Diethylmalonate in diethylethylmalonate	137
(3) 2-Bromopentane and 3-bromopentane	115
(4) 2-Pentanol and 3-pentanol	137
(5) N-(3-hydroxyethyl) phenylacetamide in the presence of ethanolamine and ethylphenylacetate	139
(6) Stigmasterol in soybean sterol mixtures	64

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PATENTS

Infrared absorption data have legal status in the prosecution of patent applications on antibiotics of unknown structure⁸⁵ as well as in the control tests discussed above. Spectra and listings of absorption bands are accepted in patent claims as a means of defining the active compound. This practice represents acceptance of the contention of Gore and Petersen⁵⁰ that an infrared spectrum fingerprints a compound to give above-average assurance of identity, except for some high molecular weight substances.

In a practical and a humane sense this approach to defining a compound of unknown structure in patent applications has two advantages. It helps to ease the burden of the patent examiner in comparing the descriptions of antibiotics in different applications. At the same time, the practice is in accord with the basic U. S. Patent Office tenet that patent protection should aid and stimulate the inventor in the public interest.

The use of infrared spectra in patent applications posed problems analogous to those associated with the adoption of infrared identity tests by The Pharmacopeia of the United States, *vide supra*. Interestingly, the telling stimulus for finding an answer to the problem originated with patent examiners⁸⁵ who found themselves confronted with spectra differing in dimensions, coordinates, and spectral range. This situation, which made direct comparisons of spectra difficult even for expert spectroscopists, was resolved by an informal study led by Mr. Donald Levy. Spectroscopists in industry and government laboratories contributed ideas and data. The ultimate result was tacit acceptance of the unofficial format recommended by The Subcommittee on Standard Data, A.S.T.M. Committee F-13. The letter to the Commissioner of Patents suggesting this format is reproduced below, and Figure 7-5 shows a spectrum of porfiromycin,¹⁴ illustrating this format.

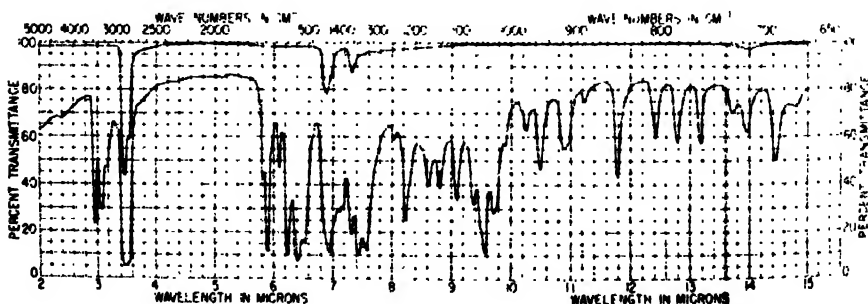


FIGURE 7-5. Informally accepted format for antibiotic spectrum in patent application porfiromycin in mineral oil mull.

“Commissioner of Patents
U. S. Department of Commerce
Patent Office
Washington 25, D. C.

**Re: Recommendation of Standard Format for
Presentation of Infrared Data**

“It was suggested that the Standard Data Subcommittee of the American Society for Testing Materials Committee E-13 on Absorption Spectroscopy recommend a single format which would be generally acceptable to spectroscopists.

“The Subcommittee discussed this problem at its meeting in Columbus, Ohio, June 18, and through extensive correspondence in the months following. A format was proposed and submitted for letter ballot approval of the Subcommittee on September 8. The format was approved by 79% of those returning ballots.

Format for Presentation of Infrared Data in Patent Applications

“1. The abscissa shall be linear in wavelength. One micron shall equal five-eighths inch so that a spectrum from 2 to 16 microns will be eight and three-quarters inches long. This length will permit reproduction of the spectrum lengthwise on a standard 8½ × 11 sheet or on a standard 8 × 10 photographic print.

“2. The ordinate shall be linear percent transmission or transmittance. The height will result from proper reduction of abscissa length of records from Perkin-Elmer, Baird, and Beckman spectrophotometers and will be about two and one-half inches.

“3. The grid of lines marking wavelength and transmittance should be spaced as follows:

a. The intervals between wavelength grid lines should be no less than 0.2 micron nor greater than 1.0 micron.

b. The intervals between transmittance grid lines should be no less than 5% transmittance and no greater than 20% transmittance.

“4. The spectrum should have a frequency scale printed across the top of the chart.

“The most serious point of controversy in the recommended format was the selection of linear wavelength rather than linear frequency for the abscissa. The percentage of data published in linear frequency seems to be increasing slightly and recently the British Chemical Society established a standard format using linear frequency.

“In spite of this, the Subcommittee feels that linear wavelength is definitely more generally acceptable in this country at the present time and actually 88% of the Subcommittee members voting on this format accepted the linear wavelength abscissa.

Standard Data Subcommittee
American Society for Testing
Materials Committee E-13*

Patent No. 2,482,055, “Aureomycin and Preparation of Same,” B. M. Duggar, September 13, 1949, contained a listing of infrared absorptions and has served as a model for many subsequent applications. A portion

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of the specifications in the Duggar patent is given below. In a decade, the practice has shifted toward a tabular listing of bands with less attention to structural interpretations.

"Characteristic infrared absorption spectra taken on a sample of the hydrochloride salt mulled in hydrocarbon oil show the following features: an O—H or N—H absorption band near 3295 cm^{-1} , phenyl C—H absorption at 3050 cm^{-1} , a possible amide carbonyl at 1665 cm^{-1} , a possible C—C stretching frequency at 1615 cm^{-1} , a possible N—H bending vibration at 1575 cm^{-1} , a para substituted phenyl absorption near 1523 cm^{-1} , a possible R—CH—CH—R, CH bending vibration at 969 cm^{-1} , and perhaps a para phenyl band at 840 cm^{-1} with sufficient additional substitutions (3 symmetrical) as shown by absorption at 851 and 863 cm^{-1} .

"The infra red absorption spectra of the hydrochloride salt in mineral oil show many other unassignable absorption bands, particularly in the region from 650 to 1350 cm^{-1} , sometimes called the "fingerprint" region of the infrared spectrum. The absorption curve in this region is shown in Figure 1 of the accompanying drawing. These absorption bands show that the antibiotic substance of the present invention is different from any previously described antibiotic material.

"Similarly to the above, the free base shows a strong O—H or N—H absorption band near 3420 cm^{-1} , most probably an O—H absorption, and other O—H or N—H absorption bands between the range 3200 to 3300 cm^{-1} . The absorption curve also shows a phenyl C—H absorption band at 3050 cm^{-1} , a possible amide carbonyl at 1643 cm^{-1} , a possible C—C stretching frequency at 1609 cm^{-1} , a possible N—H bending vibration at 1580 cm^{-1} , a p-substituted phenyl absorption near 1523 cm^{-1} , a possible R—CH—CH—R, CH bending vibration at 969 cm^{-1} , and a p-phenyl band at 825 cm^{-1} , with additional substitutions at 844 cm^{-1} , and 867 cm^{-1} , as shown in the curve of Figure 11. Additional characteristic absorption bands are also shown in the range 650 cm^{-1} to 1350 cm^{-1} in Figure 11."*

Levy and Wendt⁸⁵ also proposed a practical means for handling applications on high molecular weight antibiotics whose spectra may lack clarity and uniqueness. The examiner might properly accept the omission of an infrared spectrum when informed that, in the opinion of an expert spectroscopist, the spectrum is not a good identifying characteristic for the material in question. This point of flexibility strengthens the contribution of infrared data in making patents valuable technical literature. Certainly the unofficial acceptance of a format for presenting spectra in patents should be encouraging for groups striving for wider standardizations.

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CHAPTER

8

Application of Infrared Spectroscopy to Polymers

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INTRODUCTION

Infrared spectroscopy is including an increasing number of challenging polymer problems within its domain. In fact, infrared spectroscopy is more widely used in solving polymer problems than any other type of problem to which the infrared technique is applicable. Infrared has been used to characterize the chain structure of polymers and has led the way in interpreting the reactions of multifunctional monomers including rearrangements and isomerizations. The end groups, branches, crosslinks and other structural manifestations of the chain have been detected and identified by infrared spectroscopy. Since polymer systems are multicomponent, infrared has been widely used as a semiquantitative tool to measure end groups, isomeric composition or stereoregularity, copolymer composition, additives, fillers, branches and crosslinks. The examination of the configuration and conformation of polymer chains requires special infrared techniques, but with these techniques, infrared has been a valuable supplement to x-ray, optical rotatory dispersion, and NMR methods.

Polymeric systems present a herculean task for infrared spectroscopy. The infrared spectrum is rich due to the great diversity of structure in a polymer chain. The chain often is split by branches, entangled by crosslinks, and distorted by structural variations of the repeat unit. If the chain is free of these complications, the constancy of structure encourages crystallization; a two-phase system disturbs the infrared spectrum. The commercial polymers are further confounded by chemicals added to improve

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the weatherability, processibility, stability, etc. Fillers (up to 80% by volume) improve the mechanical properties and lower the cost of the polymeric articles, but confuse the spectrum. All of these factors interfere with attempts to characterize the polymer and the structure by infrared spectroscopy.

Although the infrared spectra of polymers are complicated, this does not deter the demands made on the polymer analyst by his colleagues. The simplicity of obtaining the spectra and the ready availability of inexpensive spectrophotometers encourage the polymer chemist to turn first to infrared spectroscopy to identify and characterize his polymer sample. The so-called "infrared expert" is continually being approached to explain the presence or absence of "new" bands and to act as a guide through the maze from spectra to structures. The spectroscopist is also asked to identify polymer samples, additives, and sources of the polymer. This chapter is written to aid the "uninitiated" in attempting to untangle the spectra of polymeric systems.

THEORY OF POLYMER SPECTRA

The spectrum of a simple macromolecule in a given state and free from extraneous impurities is characterized by its simplicity. In spite of the large number of degrees of freedom, very few infrared bands are observed. Polyethylene, for example, exhibits only five infrared fundamental bands. The bands are usually broad and diffuse with no rotational fine structure.

The first and most obvious question which must be asked is what is the relationship between the spectrum of a simple molecule and the chemical repeat unit as part of a chain of similar units? In general, for polymer molecules with large complex repeat units like cellulose and polyethylene terephthalate, the differences between the spectra of the monomer and the polymer are quite small. Hence, vast collections of infrared spectra of organic molecules are used in interpreting the spectrum of a polymer in terms of its organic functional components. On the other hand, for simple polymer molecules such as polyethylene and polyoxymethylene, the spectra of the monomer and the polymer are very different.

The interpretation of the vibrational spectrum of an isolated repeat unit or monomer generally has been approached in two ways. First, by performing a normal coordinate analysis,¹⁻⁹ the energies of the vibrational normal modes of simple molecules are calculated. If the proper structural model and parameters are used, the frequencies calculated will agree with the experimentally observed frequencies and constitute evidence in support of the structure. For complex molecules the theory applies, but the computational effort is prohibitive.

In this case the second and most popular method of interpreting the spectrum of a molecule is used - structure-frequency correlations. These correlations are possible because the vibrational modes of a complex molecule fall into two classes, "intragroup" modes and "skeletal" modes. There is a wealth of spectroscopic evidence to support the assumption that these two classes are distinct; that is, the interactions of the "intragroup" modes with neighboring groups are generally small. These "internal" modes generally have a characteristic frequency range irrespective of the molecular framework to which the group is attached. Empirical studies of these group frequency variations in a series of molecules have led to useful structure-frequency correlations^{6,25} and aid in the interpretation of the spectra of a new molecule. The "skeletal" modes generally result from extensive interaction of the modes with the molecular framework, and are characteristic of the particular molecule. Hence, these "external" modes are not useful for correlation purposes, but do "fingerprint" the spectrum of the particular molecule making it possible to identify almost any molecule. Extensive collections of spectra are used to identify an unknown sample (see Chapter 6).

Similar considerations of "internal" and "external" modes apply to the study of the spectrum of macromolecular repeat units. The lattice couples the chemical repeat units so they behave as coupled harmonic oscillators. The vibrational pattern depends on the number of coupled oscillators or cells, the normal modes of an isolated repeat unit, and the extent of coupling of the vibrational modes with other repeat units.¹³ For N coupled cells containing M atoms, there are $3NM$ degrees of freedom. The three translational degrees of freedom give null vibrations and the rotation of the polymer molecule about its own axes can be ignored, so $3NM - 4$ normal modes are important.

The salient features of the polymer spectrum may be demonstrated by analyzing a uniform one-dimensional lattice of point masses elastically bound to each other.¹⁴ The N -frequencies for a linear chain of N atoms acting as parallel dipoles with fixed ends (including only nearest neighbor interactions) are given by the following equation:

$$W_K^2 = W_0^2 + W_1^2(1 + \cos \theta), \quad \theta = \frac{k\pi}{N+1}, \quad k = 1, 2, 3, \dots \quad (8-1)$$

where W_0 = frequency of uncoupled mode, and W_1 = interaction parameter. Thus, for this model W_K is a function of the phase (θ) only. Each of the modes for an isolated monomer generates N bands in the chain of N units. If the interaction parameter W_1 for the mode is small, all of the normal vibrations fall in the neighborhood of W_0 and a "characteristic" polymer group frequency is observed. This is the case, for example, with the carbon-hydrogen stretching modes which occur at the same frequencies irrespective

of the polymer. For large W_1 , a wide range of frequencies can occur and a "skeletal" frequency is observed. Snyder¹²² has observed the CH_2 rocking vibrational band series for $\text{C}_{24}\text{H}_{50}$ (triclinic form) at -160°C . If the square of the observed frequency is plotted against $1 + \cos \theta$ as shown in Figure 8-1, there is good agreement with the behavior expressed by the above

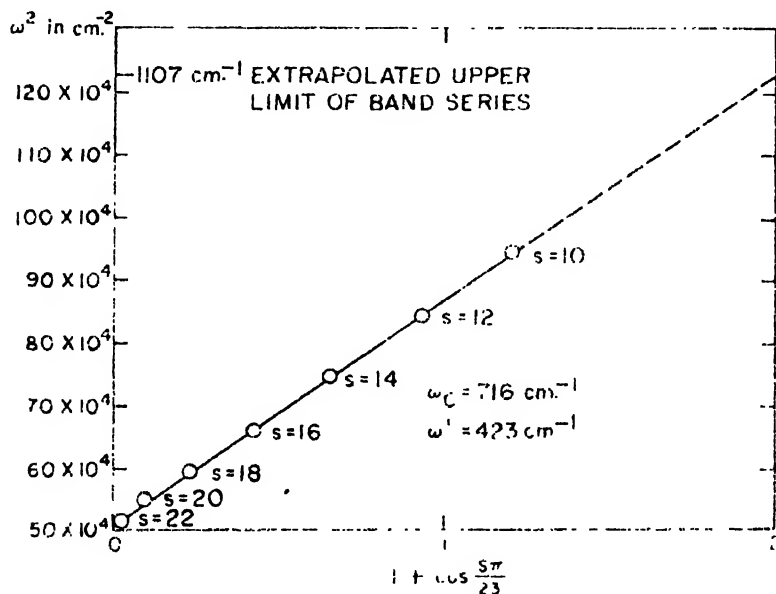


FIGURE 8-1. Square of the observed CH_2 rocking vibrational bands for $\text{C}_{24}\text{H}_{50}$ plotted against $\left(1 + \cos \frac{s\pi}{23}\right)$, corresponding to a fixed end model with 22 coupled dipoles.

equation. Equation 8-1 also describes quite well the frequencies of the CH_2 twisting vibrational band series measured by Aronovic³ for sixteen different n -aliphatic acids for which N assumes values between 8 and 34. The square of the frequency for 146 absorption bands is plotted against $1 + \cos \theta$ in Figure 8-2.

Examination of Equation 8-1 indicates that as N becomes infinite, only one infrared active mode exists, the other $N - 1$ modes being inactive. Hence, a band present in the isolated repeat unit may appear as a single infrared band for the infinite polymer chain. The shift in frequency of the absorption band in going from monomer to polymer will be determined primarily

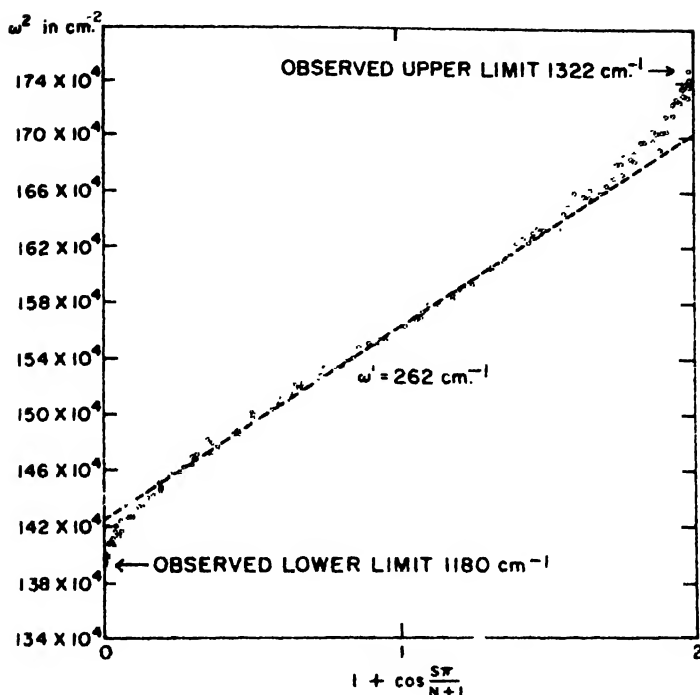


FIGURE 8-2. Observed progression band series for n -aliphatic acids $\text{CH}_3(\text{CH}_2)_N\text{COOH}$. The diagram shows the square of the frequencies

plotted against $1 + \cos \frac{5\pi}{N+1}$ for 146 bands.

(Ref. 418)

by the extent of coupling. This shift in frequency is illustrated by the $\text{C}=\text{O}$ frequencies from stereo-regular polyvinyl formate.¹¹⁵ The carbonyl str frequency is at 5.665μ (1765 cm^{-1}) in the monomer and at 5.74μ (1740 cm^{-1}) in the polymer. The ester $\text{C}-\text{O}$ shifts from 8.000μ (1250 cm^{-1}) to 8.621μ (1160 cm^{-1}) in going from monomer to polymer modes.

Normal coordinate calculations have been made for the infinite polyethylene chain⁷² to define the variation of frequency with phase angle. The results are shown in Figure 8-3. For an infinite chain, the infrared active modes have a phase 0 and π ; the intercepts constitute the only active modes, and are compared with the experimentally observed. Using the appropriate relationship for the phase angle, the infrared spectra of all lower homologs may be obtained by drawing lines parallel to the frequency ordinate for the appropriate phases.

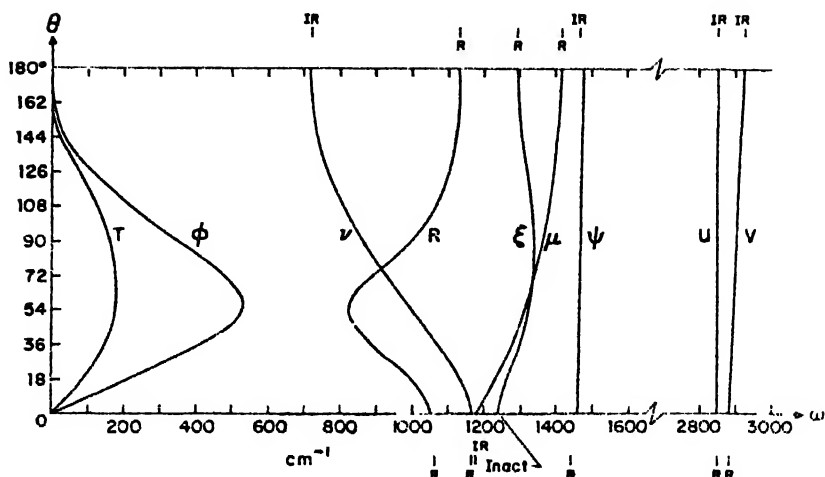


FIGURE 8-3. Calculated vibrational spectrum for polyethylene. Experimental values are indicated at both terminals of each mode.

The shift in frequency in going from an isolated chemical repeat unit to oligomer to polymer chain has satisfactory theoretical basis for the simple polyethylene case. It is observed that some of the "intragroup" modes (carbon-hydrogen str modes) are not affected by the change in phase and hence appear at a characteristic frequency. But the other eight modes have "coupling dependent" frequencies. The coupling can cause a shift in frequency of a few hundred wave numbers as observed for the methylene rocking mode.

Several conclusions can be drawn from these studies which are applicable to the spectra of polymer chains in general. First, structure-frequency correlations are useful in the infinite polymer chain, in those cases where coupling is very small. This restriction is similar to the requirement for good structure-frequency correlations for organic molecules, and so these correlations should be applicable to the analysis of polymeric spectra if used with extreme care. If the chemical repeat unit is complex, the interaction forces between repeat units will be relatively minor and the spectrum of the chemical repeat unit will resemble that of the isolated monomer. For cellulose, for example, the spectrum of an oligomer of five units is nearly the same as for cellulose.

The second conclusion that may be drawn is that for strongly coupled modes for which a characteristic frequency does not exist, the shift in frequency should be determinable by comparing a similar polymer or a series of homologs. Since a relatively simple relationship exists between

the shift in frequency and the number of units in the chain, homologs may be used to determine the extent of coupling by extrapolations to the corresponding frequency in the infinite polymer chain. This is illustrated by the work of Snyder¹²² in which he was able to assign correctly an infrared band in polyethylene by extrapolation of his extensive data on paraffins. In general, however, such homolog data are not available and other techniques must be used in order to obtain reliable structural information from the polymeric spectra.

SAMPLING TECHNIQUES

Polymers are encountered in a variety of solid forms including fibers, foams, films, coatings, finishes, powders, flakes, and massive objects. All of these forms present infrared sampling problems. The fibers are highly oriented and have insufficient diameter for adequate absorption except when an infrared microscope attachment is used. A foam is very nonuniform. A film is usually biaxially oriented and often of improper thickness to make adequate specimens. Coatings and finishes are difficult for transmission spectra but reflectance spectra can be used unless the coating is on a large object. Massive objects such as molded pieces present difficulties which are obvious.

The desire is to put the polymer in such a form as to obtain high quality spectra with ease, rapidity, and a minimum of interference. A number of sampling techniques have been used with the nature of the specimen generally suggesting one or more methods to be applied. However, various disadvantages are associated with each technique so the type of information desired often dictates the method. Identification of a polymer sample requires a quality spectrum free from extraneous bands. Qualitative structural studies require a sample of adequate thickness to yield strong bands in the region of interest. This may demand an extremely thin or thick sample. Quantitative infrared measurements require a uniform, homogeneous sample, free from orientation.

The available techniques can be summarized briefly as follows:

- (1) Films
- (2) Solution in liquid solvents
- (3) Mulls (Nujol, hexachlorobutadiene, perfluorokerosene)
- (4) Alkali halide disks
- (5) Reflectance measurements

An extremely simple technique for obtaining a film for the infrared spectrum of a crystalline polymer consists in melting the substance between two salt plates and allowing it to cool to a fairly uniform, transparent film. For polymers yielding a self-supporting film, compression molding in a

hydraulic press yields quality films. These techniques minimize the handling, give quality spectra, show all the band structure, and simplify sample storage and recovery. Disadvantages include: polymorphism, alterations associated with instability to melting, oxidation and thermal degradation, loss of information concerning crystallinity and orientation in sample prior to melting. The compression-molded films are often adequate for quantitative infrared spectroscopy since they are fairly uniform and thickness is easily and accurately measurable.

Films may be obtained by dropping or spraying a solution containing the polymer onto a window which has been heated to a temperature above the boiling point of the solvent. Films may also be cast from solution by evaporation of the solvent in a partial vacuum. This method is laborious and time consuming, but extremely useful when a suitable solvent can be found. For polymers, the solution process is slow, often requiring elevated temperature. Extremely dilute solutions are obtained requiring an extended evaporation period. Disadvantages include: degradation of polymer in solution process, difficulty of removing solvent, and loss of information about sample prior to solution.

Films may be obtained from massive objects by microtoming, slicing, or machining. This method is demanded for infusible and insoluble polymers like polytetrafluoroethylene. This method has the advantage of yielding information about the sample in its end-use state allowing measurements of crystallinity, orientation, and degradation. Disadvantages include: non-uniformity of samples, excessive scattering, introduction of orientation and small samples requiring a beam condenser.

Polymer solutions have not been as widely used to obtain the infrared spectra of polymers as for other solid substances. For crystalline polymers, this technique suffers primarily from the lack of solvents for polymers at room temperature. In addition, the shifts of absorption bands and interfering absorptions discourage use of solvents for polymer systems. For amorphous polymers, the solubility problems are not so serious and solutions may be used successfully.

Since solvents are often unavailable, the mull technique finds considerable favor for polymeric systems. In addition to the mulling agent, Nujol, hexachloro-1,3-butadiene and perfluorokerosene have been used due to the large number of substituted hydrocarbon polymers. The usual disadvantages of this technique, including band interferences, grinding effects, orientation effects, loss of sample, and excessive scattering limit the technique considerably for polymers.

The alkali halide disk technique has found considerable use for polymeric substances. The dispersal of a polymer sample in an alkali halide matrix and compression into a thin transparent wafer with a hydraulic press gives

better quality spectra than many of the techniques above. The size of the particles, both the matrix and the sample, have an important effect on the quality of the spectra. The Christiansen effect can occur in finely ground powders or suspensions with a resulting shift of absorption maxima. Polymers ordinarily do not interact with the matrix material, or form mixed crystals so some of the difficulties encountered in other solid materials are avoided. Considerable scattering does occur in the short-wavelength region because of the size of the polymer particle.

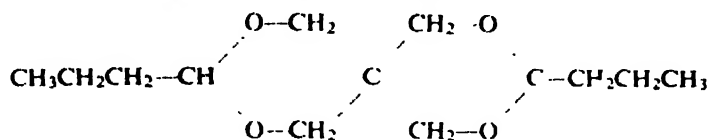
One of the newest and potentially most useful techniques is attenuated total reflectance. Totally reflected infrared radiation within a specially fabricated germanium piece interacts with a material on the surface yielding a spectrum of the surface material.³⁶⁻⁴⁸ It is particularly useful for studying materials whose spectra cannot be readily measured in transmission. The major sample requirement is close contact of the sample with the reflecting surface of the prism. This is no problem with liquids or soft or rubbery materials. With harder samples, a wetting agent may be applied. The major advantage is the possibility of obtaining the spectra of polymer samples independent of the sample thickness, thus eliminating the necessity of working the sample. The principal disadvantages are the appearance of bands due to chemisorption and difficulty with quantitative analysis. See Chapter 15 for a comprehensive discussion of attenuated total reflectance (ATR).

CHARACTERIZING MACROMOLECULAR STRUCTURE

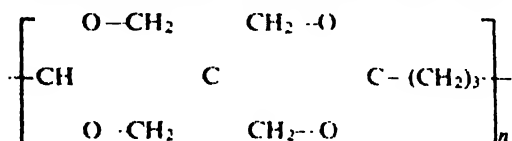
Infrared spectroscopy is a most elegant tool for defining the chemical structure of a polymer chain. The structure problems are complex and the potential number of alternate structural possibilities may be extremely high. For polyalloocimene, ten different chain structures are possible. The methods of establishing the structure of a polymer are based on a comparative analysis with (1) synthetic or natural polymers, (2) oligomers or homologs, (3) model compounds, and (4) general structure-frequency correlations.

Ideal model compounds for polymer use are other chain molecules with similar structure and coupling. Natural polymers with their regular structure make excellent model compounds. Synthetic polymers are also useful when the structure of the polymer is well established.¹ For studies of unsaturation in polybutadiene,¹¹³ the *cis* fraction of chicle rubber was used as a model for the *cis*-1, 4 unsaturation. Balata and Gutta-percha constituted model compounds for the *trans*-1, 4 unsaturation. Studies of synthetic pure *cis*-1, 4 polybutadienes have verified the earlier results¹⁰ using these natural polymers. Recent studies⁸⁷ of the carbon monoxide-formaldehyde copolymers were aided in characterizing a part of the structure of the chain by

a model structure for the polymer obtained by polymerization of acrylic anhydride.⁷⁹ The bands at 5.525μ (1810) and 5.602μ (1785 cm^{-1}) for the anhydride compared with 5.525μ (1810) and 5.745μ (1740 cm^{-1}) for the polymer indicated the hexatomic ring structure predominated at 35°C polymerization temperature. At higher polymerization temperatures, the polymer obtained has bands at 5.377μ (1860 cm^{-1}) and 5.618μ (1780 cm^{-1}) indicative of a pentatomic anhydride ring structure. A 3, 5-disubstituted nortricyclene model compound has a band at 12.4μ (806 cm^{-1}) in common with poly (bi-cyclo [2.2, 1] hepta-2, 5-diene) indicating the predominance of the nortricyclene ring structure.⁴² The spectra of the model compound



indicates the poly(piroacetal resin contains the dual-ring chain structure



as well as the isolated ring.²⁴ Many examples of this kind could be mentioned.

APPLICATIONS OF IR SPECTROSCOPY TO POLYMER STRUCTURE ELUCIDATION

The complicated spectra of the multicomponent polymer system does not limit the areas of application of infrared molecular analysis; it emphasizes the need. The areas of application include end groups, chain structure, changes undergone in polymerization including isomerization, rearrangements, branching, crosslinking; and the reactions of polymers including curing, vulcanization, oxidation, and degradation. A brief outline of these areas of application reveals the special methods and techniques.

End Groups

The nature of the initiation and termination steps in the free radical polymerization process determines the structure of the end groups; the infrared evaluation of the structure of the end groups reflects the nature of these polymerization steps. The number of end groups in a polymer of high molecular weight is low and normal chemical techniques are sometimes not practical. The infrared bands of the end groups are revealed by their sensitivity to molecular weight; that is, bands which vary in intensity

when a high molecular weight polymer is compared with a low molecular weight sample. Difference spectra, using samples of widely differing molecular weight, amplify the end-group bands. A disproportionation reaction as the termination step in the polymerization of isobutylene was mirrored in the vinyl end groups²⁷ (bands at 6.09μ (1642 cm^{-1}) and 11.1μ (901 cm^{-1})),²⁸ while chain transfer (transfer of growing chain to another chain) was indicated for copolymers of ethylene and α -olefins by the presence of vinylidene groups.⁷

For condensation polymerization, the end-group structure is related to the monomer structure as no initiating agent is added. In the condensation copolymerization of dihydrosiloxane with excess acetylene, olefin end groups were detected by bands appearing at 6.270μ (1595 cm^{-1}) and 3.279μ (3050 cm^{-1}); with excess dihydrosiloxane, silane end groups by a band at 4.762μ (2100 cm^{-1}).¹⁰⁹

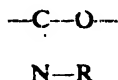
The reactions of end groups can be followed by infrared spectroscopy. For polyoxymethylene, the esterification of the hydroxyl end groups is followed by the decrease in intensity of the hydroxyl band at 2.9μ (3448 cm^{-1}) and the appearance of new bands at 5.69μ (1757 cm^{-1}) and 5.76μ (1736 cm^{-1}) due to the ester groups.⁶⁴ The aqueous polymerization of tetrafluoroethylene initiated with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in neutral or weak acid solution leads to a polymer containing carboxyl end groups. The conversion of these end groups to the sodium salt and its pyrolysis to the terminal olefin was followed using the infrared absorption technique.¹⁵

Chain Structure of Homopolymer

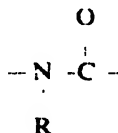
The chain structure of a polymer is the most important factor in determining the chemical, physical, and mechanical properties of a composition. The chain structure may be complex when a multifunctional monomer is polymerized and several different polymerization reactions may occur; usually one mode of polymerization predominates. The infrared spectrum of the polymer obtained by the polymerization of acetaldehyde by the "freezing" method, or with catalyst systems, indicated an acetal type polymer by the comparison of the spectra with paraldehyde and metaldehydes. The 7.25μ (1378 cm^{-1}) methyl band and an ether band at 9.09μ (1100 cm^{-1}) described the structure for the repeat unit. Polymerization of acetaldehyde under high pressure gave a highly unsaturated olefinic type polymer; probably due to hydrolysis of the hydroxyl groups. Ionic polymerization of acetaldehyde with sodium amalgam gave a polyvinyl alcohol type polymer: presence of a hydroxyl band at 3.00 to 3.13μ (3333 to 3195 cm^{-1}) and absence of ether type bands.⁵⁶ The type of chain structure is easily determined by comparison with spectra of sample polymers. An excellent selection of quality spectra of this type is due to Nyquist.¹⁰²

The chain structure need not be a single type as illustrated above, but may be very complex due to side reactions occurring during polymerization. For the polymerization of suberaldehyde, simultaneous reactions such as aldol condensation, a Tishchenko reaction, and a cyclic polymerization involving the carbonyl group and a linear polymerization through the carbonyl group could produce an extremely complex chain structure. Comparisons of model polymer chain structures and their anticipated spectra indicated that the aldol condensation reaction had occurred. Additional bands in the spectrum were contributed by products resulting from isomerization and hydrolysis of the aldol product.⁶⁷

Isomerization of the monomer during polymerization complicates the chain structure. Fortunately, the spectra reflects these complications. The isocyanates have two isomeric forms capable of polymerizing. One form gives a polyacetalic chain structure of the type

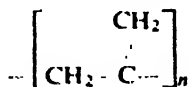


and the other form a disubstituted amidic type

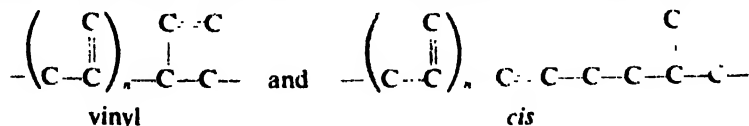


of chain. Comparisons with the spectra of low molecular weight analogs indicated that the *n*-butyl isocyanate polymer was of the disubstituted amide type (very intense band at 5.89μ (1698 cm^{-1})).⁹⁶

Isomerization of the chain occurs for the polymer obtained from the polymerization of allene. In addition to the vinylidene type of chain structure



the spectra indicated considerable rearrangement had occurred of type



where the *cis* unsaturation was indicated by the presence of bands at 11.31μ (696 to 708 cm^{-1}) and the band at 10.07μ (993 cm^{-1}) was indicative of vinyl unsaturation. Mixtures require extraordinary attention since the relative intensities of the bands do not necessarily reflect the importance

of the contributing structure to the properties of the polymer sample and "ghosts" of this type frustrate and infuriate attempts at structure-property correlations.

Chain Structure of Copolymers

The chain structure of copolymers may be tested by comparison of the spectra with the spectra of the respective homopolymers. This will suffice to indicate the general nature of the chain structure. The distribution of sequence lengths (number of successive identical monomer units between comonomer units) determines the properties of a copolymer. For example, the physical mechanical properties of a block copolymer and a random copolymer are different. A block copolymer appears spectrally similar to a physical mixture of the two homopolymers (allowance being made for crystallinity differences). A random copolymer, because of the short sequence lengths, may give rise to bands not observed in the homopolymers, or bands may be absent in the random copolymers which are found in the homopolymers. A random copolymer of ethylene-propylene has no band at 8.666μ (1154 cm^{-1}) that is found in the spectra of amorphous polypropylene and block copolymers of ethylene-propylene.⁵ The change in intensity and frequency of bands in copolymers compared to homopolymers is a result of the change in the extent of coupling. The largest change in coupling is for a copolymer chain consisting of alternating monomer units — a one-to-one alternating copolymer. For copolymers of ethylene, a shift in the methylene rocking mode from 13.9μ (720 cm^{-1}) for random distribution to 13.2μ (758 cm^{-1}) for a one-to-one alternating copolymer occurs. Natta characterized his alternating copolymers of ethylene-cyclopentane⁹⁹ and ethylene-butene-2¹⁰⁰ by utilizing this characteristic difference in spectra. Bands characteristic of various triads (three successive monomer units) may be observed as in the vinylidene chloride and vinyl chloride copolymers. Here, the bands characteristic of the following triads are assigned:

—VDC—VC—VDC—	8.354μ (1197 cm^{-1}),
— VC—VC—VDC—	8.097μ (1235 cm^{-1}),
— VC—VC—VC —	8.019μ (1247 cm^{-1}).

Bands characteristic of all the possible lengths are certainly present in the infrared spectra, but because of the small coupling frequency shift they are lost in the shadows of the stronger bands characteristic of longer or shorter sequences. High resolution spectrophotometers will aid these studies. If low temperature is utilized (to sharpen the bands), more information is available to the diligent.

Branches

Branches on the polymer chain occur since the growing free radical chain is extremely reactive and can react with the initiator, monomer, and even

with itself by the "backbiting" process. These branches may be extremely long (perhaps as long as the molecule itself) or very short. The number and length of the short chain branches in polyethylene affect the physical properties considerably. For polyethylene, methyl groups are detected by characteristic bands at 7.25μ (1378 cm^{-1}) and 3.378μ (2960 cm^{-1}). Infrared measurements by Fox and Martin⁴¹ in 1940 indicated that the intensity of the methyl carbon-hydrogen str band at 3.378μ (2960 cm^{-1}) was too great to be due to end groups only. Absorption in the 13μ (720 cm^{-1}) region of the polyethylene spectrum has been attributed to short chain branches.¹⁰ The wavelength shift for various branch lengths as defined by various homopolymers of the α -olefins may be improper due to coupling of the methyl group with adjacent groups. However, copolymers of α -olefins with excess ethylene give rise to isolated branches and should be excellent model compounds. The methyl rocking band is found at 1028μ (973 cm^{-1}) in the spectrum of polypropylene and a very weak band (ethyl band) at 10.84μ (922 cm^{-1}) is observed for polybutene. A band at 11.18μ (894 cm^{-1}) occurs for alkyl branches greater than C_4 . The methylene rocking mode depends on the lengths of successive methylene groups both in the branches and main chain. Work by Sutherland *et al.*¹²⁴ on low molecular weight liquid hydrocarbons indicated ethyl and propyl groups give rise to methylene rocking bands at 12.99μ (770 cm^{-1}) and 13.51μ (740 cm^{-1}). Butyl 13.70μ (730 cm^{-1}) amyl 13.79μ (725 cm^{-1}) and hexyl branches absorb at 13.89μ (720 cm^{-1}). The band at 12.99μ (770 cm^{-1}) observed in polyethylene is attributed to ethyl groups,¹¹⁶ and a band at 13.42μ (745 cm^{-1}) to butyl groups,¹¹⁸ but these bands appear as slight inflections on the shoulders of the very intense methylene band due to very long sequence of methylene groups in the chain at 13.89μ (720 cm^{-1}). Polyethylene has no bands at 10.28μ (973 cm^{-1}) and 8.69μ (1151 cm^{-1}) which are indicative of the pendant methyl but these bands are characteristic of this group as indicated by studies of polypropylene.^{9,131}

Branches may also result from side reactions. The spectrum of the polymer obtained by the polymerization of 3-methyl butene-1 using the Ziegler-Natta catalyst system showed a band at 13.16μ (760 cm^{-1}) indicating the presence of ethyl groups in the polymer. These groups apparently arose by displacement of the ethyl from the triethyl aluminum during polymerization.⁶² Branches may also be detected but no specific indication as to their nature for the 1-olefin polymers if bands are observed at 12.99μ (770 cm^{-1}) and 13.57μ (737 cm^{-1}) which have been attributed to the presence of adjacent tertiary carbons.⁵⁷

Crosslinks

The introduction of crosslinks (chemical coupling of polymer chains) gives many useful properties to polymer systems, including hardness and

low flow. For linear polymers, crosslinks are undesirable because of their effect on the processibility of the polymer. The melt viscosity is the property most affected by the introduction of crosslinks but it yields no information about the nature of the crosslink.

The infrared detection of crosslinking is difficult. The structure of the crosslink is usually very similar to the main chain, so no new infrared bands result. For these systems, it is necessary to deduce the nature of the crosslinks by the type of changes occurring in infrared bands of other reactive groups; for hydrocarbon systems, it is possible to follow the decrease in unsaturation.⁸ For crosslinking occurring as a result of oxidation, the broad ether band at 8μ (1250 cm^{-1}) to 8.5μ (1176 cm^{-1}) reflects presence of crosslinks in polyethylene.

When the chemical structure of the crosslinks is different from the polymer chain, the problem is simplified. Structural differences between the main chain and the crosslinks arise when a specific crosslinking agent is added to the polymer. Polystyrene is crosslinked by copolymerization with divinyl benzene and the crosslinking is detected by appearance of bands characteristic of trisubstituted benzene rings.¹²⁶

INFRARED CHARACTERIZATION OF THE CHEMICAL REACTIONS OF POLYMERS

Since the chemical reactivity of a polymer is important in determining its usefulness commercially, one must be able to study these reactions. The ability to crosslink rapidly giving a rigid product characterizes thermosetting resins. The vulcanization of rubbers is a well-known process for obtaining the proper elastomeric properties. Inertness to atmospheric conditions provides many uses for the proper resins as coatings and finishes.

Infrared spectroscopy has been used in the study of polymer reactions to identify the products, measure the extent of reaction, and follow the rate of the reaction. Infrared studies are particularly convenient as the polymer can be examined in its end-use form. Infrared scans of solid films before and after chemical reaction facilitate detection of new bands and hence new products. Some reactions such as thermal degradation and oxidation can be monitored in the infrared machine in two different ways: (1) difference spectra, and (2) scan of single wavelength as function of time. The rate of reaction can be increased by elevating the temperature, and a cell has been designed for this purpose.¹¹ For studies of coatings and finishes, the attenuated total reflectance attachments make sampling very easy.

The ability of infrared to identify the products of reaction is particularly useful for polymer reactions.¹¹⁷ Since polymers may be considered as large

organic molecules, the reactions are often typical of their low molecular weight analogs. In the oxidation of polyethylene⁵⁰ the peroxide intermediates can be detected at 5.634μ (1775 cm^{-1}) and the acid at 5.84μ (1712 cm^{-1}), ketone at 5.81μ (1721 cm^{-1}) and aldehyde at 5.77μ (1733 cm^{-1}). All infrared bands of unaged polyethylene are reduced with the exception of the 7.25μ (1378 cm^{-1}) (symmetrical deformation of CH_3) indicating no change in the concentration of methyl groups during the reaction in comparison with the other groups. Richards has demonstrated during degradation of polyethylene that the number of double bonds per molecule remains stationary, but changes in the type of double bonds occur as the reaction proceeds.¹⁰³

Similar studies have been carried out on the butadiene popcorn polymer. The acid, aldehyde, ketone, ester, and anhydride carbonyl bands were examined. Chain fission was found to occur without loss of unsaturation, and the mechanism for this process has been proposed by Miller.⁸⁰

Infrared studies of the reactions of polymers including grafting^{63,85,112} irradiation,^{22,30,35,36,38,77,81} thermal degradation,^{4,5,47,73,129} weathering,⁵⁴ and condensation²⁸ have been reported.

At very low conversion, a chemical reaction of a polymer may disrupt the structure and order of the chain exerting an abnormally large impact on the physical and mechanical properties. This may result in fracture or failure of the plastic object. Consequently, the early detection of a chemical reaction and a measure of its role is important in determining the lifetime of an object under a specified chemical environment. Infrared studies of samples permits the early detection of the kind of reaction occurring. The reaction inducing the formation of color in polyurethane was detected at an extremely early stage by difference spectra.⁶ This knowledge is essential to the selection of the proper kind of inhibitor to add to the polymer. The autocatalytic peroxidation with air of polybutene in the absence of special initiators⁶⁰ is another example. The analysis of ketonic carbonyls by IR complemented the chemical analysis of hydroperoxides, peroxides, "active" hydrogen, and alcohols of the oxidized product. Such studies aid in the selection of stabilizer compounds to inhibit the oxidation reaction and increase the use-time of plastics.

QUANTITATIVE IR MEASUREMENTS ON POLYMER SYSTEMS

The infrared tool is most appreciated in its role of quantitatively measuring the concentration of components of a polymer system. Ease of sampling, non-destructive nature of the test, rapid analysis, possibility of automation, simultaneous measurements, and sensitivity, contribute to the desirability of quantitative infrared measurements. Orientation, scattering,

interfering absorptions, and nonhomogeneity contribute to the difficulty of quantitative infrared measurements.

The Beer-Lambert Law

Quantitative spectral measurements assume the Beer-Lambert law holds:

$$c = -\frac{\log \frac{P_0}{P}}{ab} \quad (8-2)$$

where

c = concentration,

b = path length

$\log \frac{P_0}{P}$ = absorbance

a = absorptivity.

This is not the place to review the assumptions and approximations of this equation* but the techniques which apply to polymer systems for the measurement of the various experimental quantities will be discussed.

The measurement of the absorbance (optical density) ($\log P_0/P$) of a particular infrared absorption band is, in principle, very easy. With a double beam spectrophotometer, the P_0 is being continuously compared to P , and the chart records the difference: the logarithm of this difference is the absorbance.

However, several difficulties arise. Spectrophotometers do not deliver a monochromatic beam because of the necessity for a finite slit opening, and the absorption is spread over a band of frequencies. In the absence of other absorptions, this distortion may be corrected by integrating the area under the peak over the range of frequencies and the total absorption is approximately independent of the slit opening. Since the absorptions are not inherently sharp, the effect of the slit width becomes less important as the absorption band broadens. Satisfactory optical absorbance measurements may be obtained from "peak height" measurements (measure per cent transmission at band maximum) if the slit width is a tenth of the band width. For polymer absorptions, this is normally the case.

The "Base-Line" Technique

The scattering and reflection of radiation from a solid sample contribute to a reduction in transmission of the sample at all frequencies. But these losses are relatively insensitive to frequency. The "base-line" density technique⁵¹ empirically erases these nonabsorption losses from the radiation. A "base-line" is drawn between two selected frequencies at minimal ab-

*The Beer-Lambert law is discussed in detail in Chapter 2.

sorption intersecting both sides of the absorption band. A perpendicular line is dropped from the band maximum and the intersection of this line with the "base-line" is taken as a corrected P_0 . This procedure is not theoretically correct

$$\left(\log \frac{P_0 - S}{P - S} \neq \log \frac{P_0}{P} \right)$$

but serves as an empirical method of correcting for nonabsorption losses. The "base-line" density technique has found much favor with spectroscopists studying polymers because of its simplicity and rapidity. Experimental testing of the Beer-Lambert law is always recommended, but unfortunately often neglected.

Elimination of and Correction for Interfering Absorptions

The discussion has thus far assumed absence of interfering absorptions. Unfortunately, with polymers one is seldom so lucky. The variations in polymer structure are usually small but important and the bands are rarely widely separated. Sometimes it is possible to remove the interfering absorption by shifting it to another frequency through reaction of the functional group; the interfering unsaturation absorption can be removed by bromination in the measurement of alkyl branches in polyethylene.⁷⁵ The acid carbonyl absorption in oxidized polyethylene can be moved from the ketone carbonyl absorption by reaction with sulfur tetrafluoride.⁵²

Procedures are available to correct for the interfering absorption by measuring the contribution of the interfering absorption at the analytical wavelength. The contribution to the absorption at the analytical frequency is assumed to be proportional to the intensity of the interfering band at the band maximum. This method is not readily reproducible with high precision since a constant band shape must be assumed. The measurements are required because a structural change is assumed to occur. This structural change contributes a change in the internal environment of the sample and a change in band shape may result.

A difference spectrum is the most accurate way to eliminate an interfering absorbance; the infrared instrument itself performs the subtraction of the sample and reference absorbance at equal wavelengths. Once the nature of the interference is determined, a reference, identical to the sample except for the analytical component, can be used to subtract the interfering absorbance. Solution versus solvent is a familiar example of this technique. A film cut into a reference and a sample portion (sample being subjected to a chemical reaction) is an elegantly simple example of this technique⁷⁴ for polymer systems. The need for identical path lengths is a demanding one for solid samples, whereas a variable thickness cell or matched cells

suffice for liquids. A wedge-shaped film¹³⁸ or a bank of reference films of different thicknesses constitute simple methods of obtaining matched samples for solids. In addition to the reacted versus unreacted compensation example above, homopolymer versus copolymer, branched versus unbranched, and crystalline versus noncrystalline are useful compensation examples worthy of investigation.

Sample-Thickness Measurement

The measurement of the path lengths of the beam for a gas and liquid sample is simple. Similarly, for solid films, a micrometer measurement suffices when the samples are sufficiently thick. Mulls, KBr pellets and very thin films present a more difficult measurement. If an infrared band can be found which measures the amount of sample in the beam, the intensity of the band can be used as a measure of the thickness of the sample. The ratio of the absorbance of the analytical band to the internal thickness band should be proportional to quantity of component. The "internal thickness" band must be independent of the state (crystalline or amorphous), the method of preparation, and the relative intensity of neighboring bands. Ideally, the internal-thickness band for a polymer sample should be independent of orientation (not possible, but the dependence should be small), and should approximate the intensity of the analytical band to minimize the effects of nonhomogeneous distribution of sample in the beam.

Absorptivity Determination

The evaluation of the absorptivity for an infrared band indicative of a type of polymer structure is more demanding than the measurements of intensity of the bands and thickness of samples. The absorptivity is more sensitive to coupling than the frequencies, as illustrated by the dependence of the absorptivity on the chain length for modes which absorb at a frequency independent of wavelengths. This implies more attention must be given to the calibration process.

The methods of determining the absorptivity of an infrared band for a polymeric structure include:

- (a) Chemical analysis (titration, etc.)
- (b) Physical methods (radioactive labeling, etc.)
- (c) Model compounds
 - (1) Polymers
 - (2) Oligomers
 - (3) Low molecular weight analogs

The calibration of an absorptivity with the concentration of the component as determined by chemical analysis has limited application since only demands of convenience and savings of time would require an infrared

method. The advantage of calibration by chemical analysis is the direct correlation of absorbance with numbers of structural units. This determines the absorptivity unambiguously. The chief disadvantage is the limited availability of appropriate chemical methods. The absorptivity for the vinylidene unsaturation in polyethylene⁷³ may be determined by titration with bromine for a quantitative end-group analysis.

The infrared absorptivity may be determined by a calibration with another physical method; if another method is available such as NMR for stereoregularity or x-rays for per cent crystallinity. An infrared measurement is ordinarily not needed unless time, ease of determination, and possible simultaneous measurements are important factors. Radioactive labeling is an extremely useful method of calibrating an absorptivity for a copolymer determination for example. This method is obviously slow and expensive, but is sometimes the only method of accurately calibrating a given infrared analysis. An excellent example of the use of radioactive labeling is given by Sterling and his co-workers¹²² for the terpolymer system — methyl isopropenyl ketone, butadiene, and acrylonitrile. Efforts to determine the absorptivities by using the copolymers as model compounds failed because band intensity ratios did not remain constant in going from the copolymer to the terpolymer (probably due to coupling difference). However, by labeling the isopropenyl ketone with carbon 14 and determining the acrylonitrile by the Dumas Nitrogen determination, the absorptivities were determined directly from the terpolymer system.

Determination of Molecular Weight

Molecular weight measurements illustrate the technique involved for quantitative functional measurements with infrared spectroscopy in polymer systems.⁹⁵ The measurement of the number of end groups in a polymer molecule can be used to calculate the number-average molecular weight. These end-group analyses are particularly useful for those polymers which are insoluble and intractable, and normal molecular weight measurements by solution cannot be used. The exchange of deuterium for hydrogen in the hydroxyl groups in PET¹⁰⁶ results in a decrease in the intensity of the hydroxyl band. This decrease is measured and the sample analyzed for the amount of DHO or D₂O. These calibration techniques are ideal because they are simple and the absorptivity is correct since it has been determined for the actual polymer sample.

Lower homologs may be used to determine the absorptivity of the end groups on the infinite chain by extrapolation.⁹⁹ The value of the absorptivity usually approaches a limiting value for long chains. The intensity of the hydroxyl band in polyethylene glycol¹⁴⁰ was measured for the oligomers up to the heptamer. One observes an increase in the absorptivity up to the

limiting value of the heptamer level and this limiting value of the absorptivity is used for the calculation of the molecular weight for the polyethylene glycol system.⁸ Unfortunately, such oligomers or homologs are usually not available.

One can use a low molecular weight analog as a model compound in a few cases. For specific example of the free radical initiation of polystyrene with four-benzeneazobenzoic acid, the molecular weight and size of this end group is large and the absorptivity of a characteristic mode should be independent of its attachment to the molecular chain. The absorptivity is determined with a solution of the acid in the solvent used for the polymer system.

There are two general limitations to the molecular weight calculations from end-group analysis. The first is a limitation based on lack of precise knowledge of the polymerization process. End-group analysis assumes knowledge of number and type of end groups on a single polymer chain; either one or two groups per molecule. The presence of impurities gives side reactions upsetting this assumption.^{9b} The effect on the absorptivity of the physical state of the end groups is not usually known.

Determination of Copolymer Composition

The quantitative measurement of the composition of copolymers represents one of the most useful and also one of the most difficult infrared measurements. The measurements are needed since the differences in monomer reactivity make the composition of the polymer different from the composition of the monomer feed. The infrared measurements are formidable since the coupling phenomena affect the absorptivity and make calibration difficult. The difference in crystallinity and bonding also affects this coefficient. If the monomers are sufficiently large so coupling does not occur, a simple mixture of the monomers or homopolymers suffices to determine the absorptivities of the analytical bands. An infrared band for each component should be used, yielding an internal check of the measurements. Most often, however, coupling occurs so frequency shifts and changes in the absorptivity are observed. Copolymers may exhibit a complete range of crystallinity variations, further complicating the problem.

A most interesting example of the development of a method for determining the copolymer composition by infrared analysis is the ethylene-propylene copolymer composition analysis. Wei¹³⁷ used the ratio of the 13.9μ (719 cm^{-1}) (CH_2 rocking for long sequences of methylenes) to the 8.7μ (1149 cm^{-1}) methyl band to determine the propylene content. He calibrated his ratio using mixtures of the homopolymers in solution. Cohen²⁴ criticized Wei's method on the basis that the 8.72μ (1149 cm^{-1}) band

was a crystalline sensitive band, and proposed eliminating the two phase system by making measurements on the melted polymer using the ratio of the 7.25μ (1378 cm^{-1}) methyl band to the 6.82μ (1466 cm^{-1}) methylene band. High temperature work is slow and the temperature sensitivity of the absorptivities lowers the precision. Smith¹²³ and co-workers prepared different copolymers with carbon-14 labelled propylene which was determined by scintillation counting. The 8.70μ (1149 cm^{-1}) methyl band was used and changes in crystallinity with composition which affect the absorptivity were properly accounted.

The IR measurement of the distribution of the sequence length of methylenes in the ethylene-propylene copolymer system has been reported.¹²⁴ The 13.7μ (730 cm^{-1}) (13 successive methylenes) and the 13.9μ (720 cm^{-1}) (5 successive methylenes) infrared bands were used for this purpose. The absorptivities were obtained from low molecular weight analogs. Normal heptane and hexadecane were used for determining the absorptivity of the 13.9μ (720 cm^{-1}) band and 3-methyl heptane and 2-methyl hexane for the 13.7μ (730 cm^{-1}) band. Since these two bands overlap, the interference of the 13.9μ (720 cm^{-1}) band on the 13.7μ (730 cm^{-1}) band was removed by compensating with a wedge-shaped liquid cell filled with hexadecane. The film was then removed and the absorbance of the hexadecane at 13.9μ (720 cm^{-1}) was measured. The ratio of the absorbances of these two bands is an indication of the number of long-to-short sequences of methylenes, and the author deduced that this ratio had the proper magnitude to indicate an approximately random distribution of methylene sequences.

Another potentially useful method of analyzing the composition of a copolymer by infrared analysis is an extension of the internal thickness band technique to functionality.¹ One follows the change in the ratio of absorbance of a band characteristic of a nonreacting functional group to a band characteristic of a reacting group.⁶⁶ For the copolymerization of a polyester with styrene, the double bonds change as a result of reaction, while the carbonyl concentration remains constant. The per cent of the monomers is given by:

$$\% A = D_3/D_1 - D_2/D_1 \times 100 \quad (8-3)$$

where D_3/D_4 represents the ratio of unreacted group A to nonreactive B in the copolymer, D_2/D_1 represents the ratio of group B to group A in unreacted. This procedure is extremely simple and calibration is simplified since, for the example above, only the styrene monomer is needed for the calibration. However, no internal check of the measurements is possible unless both monomers are tested.

CONFIGURATION OF THE CHEMICAL REPEAT UNIT IN THE POLYMER CHAIN

The Favored Rotational Isomer

The configuration of a polymer chain is an important factor determining its spatial structure and significantly affects the physical and mechanical properties of the polymer. The chemically-pure structurally-ordered polymer chain has a favored rotational state. This isomer is normally found in the crystalline state. For polyethylene, it is the *trans* planar zig-zag form. For polyvinyl chloride, it is the syndiotactic planar form. For isotactic polymers with bulky side groups, it is the slightly out of plane rotation about the carbon-carbon bond, the angle of rotation depending on the size of the side group, and the nature of the intra and intermolecular forces. These stable isomers are predominant, and it is their spectra which predominate.

Less Favored Isomers and Folded Chains

However, in addition to this thermodynamically favored rotational isomer, other less favored isomers are present to distort the chain structure. For example, morphological studies^{4,5} show polymer single crystals contain a completely folded polymer chain. Although it appears to be possible to remove these folds by annealing under pressure, normal crystalline polymer samples contain folded chains.

For polyethylene, these noncrystalline folds require a minimum of 5 successive *gauche* structures (rotation about C—C bond of 120°) while the crystalline portions contain all *trans* structures. The 10.37 μ (964 cm⁻¹), 7.304 μ (1369 cm⁻¹), 7.391 μ (1353 cm⁻¹), and 7.674 μ (1303 cm⁻¹) bands are felt to be modes of the *gauche* CH₂—CH₂ units and may be assignable to the folds or other disordering in the sample. These bands are observed easily in the infrared spectrum of polyethylene single crystals and correlations of their intensity with fold period have been made.¹⁷ Polyethylene is the simplest system since the two possible *gauche* structures cannot be distinguished. For most polyvinyl systems, the two *gauche* structures are not equivalent. The bands characteristic of the less favored rotational isomers are usually "amorphous" or noncrystalline bands, and can be isolated.

Atactic, Isotactic, and Syndiotactic Polymerization

In addition to reversible rotational isomerization introduced by heating or working, the polymerization process introduces for some polymers rotational isomers of the monomer as different structural units. For isotactic polymerization, the unsymmetrical monomers attach themselves to the chain with their substituents on the same side of the plane, while in syndiotactic polymerization the monomers attach themselves to the chain with

their substituents regularly alternating on one side of the plane and the other. Unfortunately, the polymerization process is neither isotactic nor syndiotactic, but ranges from completely random to nearly pure stereoisomer addition. The mechanical properties of the polymer are determined to a large extent by the crystallinity, which, in turn, is determined by the stereoisomeric composition of the polymer chain. Highly atactic (random) polymer is noncrystalline, while highly isotactic or syndiotactic polymer may approach the theoretical crystalline limit. In this way the chain behaves like a copolymer of rotational isomers, since the isomer will not interconvert without bond breaking. Methods of determining chain configuration are therefore of importance in helping to understand properties of macromolecules.

Measurement of the Stereoisomer Composition of the Polymer Chain

The presence of rotational isomers is mirrored in the infrared spectrum by (1) appearance of new frequencies, (2) shifting of frequencies, and (3) band broadening. Methods of measuring the stereoisomer composition of a polymer chain depend on knowing the relationship between these spectral properties and isomer structure.

Infrared bands characteristic of a particular rotational isomer may be observed. The assignment of an infrared frequency to a geometric isomer may be established by (1) synthesis of polymer containing one rotational isomer, (2) correlation with rotational isomers of low molecular weight analogs, and (3) normal coordinate analysis.

The ideal method of ascertaining the spectral differences resulting from a syndiotactic versus isotactic structural change is to prepare the two sterically pure polymers and compare their spectra. This is possible for very few polymers. For polyvinyl alcohol,⁹² absorptions at 10.92μ (916 cm^{-1}) and 8.764μ (1141 cm^{-1}) were found to be characteristic of the syndiotactic structure after the isotactic polymer was prepared. For polymethyl methacrylate,¹⁰² the ratio of absorbance of the 13.35μ (749 cm^{-1}) band to the 13.21μ (757 cm^{-1}) band has been correlated with isotactic pairs, and the ratio of the 9.41μ (1063 cm^{-1}) band to the 7.262μ (1377 cm^{-1}) band has been correlated with the syndiotactic pairs.

In most cases, neither sterically pure polymer can be made. Polyvinyl chloride is such an example. The structure-sensitive bands can be determined if one has faith in the free radical polymerization theory,^{40,101} which predicts that syndiotactic propagation of vinyl chloride polymerization is enhanced over isotactic propagation by decreasing the polymerization temperature.

Comparison of the spectra of the two polymers polymerized at two temperature extremes led Fordham³⁹ to select the ratios of the absorbances

of the 15.74μ (635 cm^{-1}) to the 14.45μ (692 cm^{-1}) bands as being directly proportional to the syndiotactic/isotactic ratio, where the proportionality constant is equal to the ratio of the syndiotactic to isotactic molar absorptivities. Similar spectral assignments could be drawn from studies of other polymers.

Assignment of bands to the stereoisomers encourages their use for semiquantitative measurements of differences in the stereoregularity of polymers. Although the validity of such measurements has been questioned,³⁸ they are nevertheless playing an increasing role in studies of stereospecific polymerization. The report of the synthesis of a new stereospecific polymer⁶¹ might well give a semiquantitative infrared method of measuring stereoregularity as routinely as a method of determining molecular weight.

Stereoregularity of Polypropylene. Polypropylene is an important commercial polymer which has received considerable study towards development of a sound method of measuring its stereoregularity.

Peraldo¹⁰⁸ first observed the effect of stereoregularity on the 10.02μ (998 cm^{-1}) skeletal vibration of polypropylene. Quynn¹¹¹ related the density of the polymer sample to the absorbance of certain bands in the infrared spectrum of isotactic polypropylene using the 10.27μ (974 cm^{-1}) mixed carbon-hydrogen mode as an internal thickness band. This was followed by similar methods by Luongo⁷⁶ and Brader.¹² Luongo used the ratio of the absorbances of the $\frac{10.27\mu}{10.02\mu}$ (974 cm^{-1}) 995 cm^{-1}) bands as a measure of

the per cent atactic fraction in the sample. Brader used the $\frac{8.57\mu}{10.27\mu}$ ($1167\text{ cm}^{-1}/974\text{ cm}^{-1}$) band ratios to measure the degree of helical content (as he terms it) as opposed to the per cent isotacticity. This statement results from the observation of positive deviations from the linear relationships between the absorptions and the per cent crystallinity. The reason for such deviations is the failure of all of the isotactic polymers to crystallize. For 100% isotactic polymer, only an 80 to 85% crystallinity is obtained. In addition, the presence of stereoblock polymer further limits the attainable crystallinity. For example, the *n*-heptane soluble polypropylene fraction contains stereoblock material possessing a degree of order corresponding to 20 to 40% isotactic polypropylene.^{18,78} The crystallinity that this stereoblock polymer can attain depends on the steric arrangement and the temperature of annealing. If extremely short sequences of isotactic units are present, the polymer chain will not be able to assume the helical conformation necessary for crystallization.^{70,71} For intermediate sequence lengths, the crystallization and annealing conditions must be different due to the lower melting points of stereoblock polymers.⁹⁷ Thus, the linear relationship between the ratio of the intensity of the absorption bands

and density is a useful measure of the "effective" isotacticity from a crystallization point of view, but is not useful at either end of the isotacticity scale. The failure of these procedures was illustrated by Sihilia¹²¹ who obtained three different per cent isotacticities for three different bands, the disagreement being greatest for low tacticity. One serious drawback in the low tacticity range is the failure of the 10.27μ (974 cm^{-1}) band to behave as a true "internal" thickness band.⁶⁵

A measurement of the absolute isotactic content must measure the helical content of the polypropylene sample independent of the crystallinity.⁹⁴ Three methods are available to accomplish this type of measurement. First, the measurements can be made on an isolated band which is sensitive to the helical regions. The 8.658μ (1155 cm^{-1}) band has been given such an assignment,³⁸ but has not been used to make any tacticity measurements to date. A second technique, which has been championed by the Russians,^{19, 46, 136} is to determine the degree of tacticity on the basis of the ratio of the dichroism of the 3.418μ (2926 cm^{-1}) band to the 3.515μ (2845 cm^{-1}) band. This ratio depends on the tacticity, but is independent of the degree of crystallinity and elongation of the specimens. Finally, one can use the broadening of an infrared band⁶⁵ which is caused by the slightly different frequencies of the rotational isomers or sequence lengths.

Usefulness of Model Compounds. The elegant use of model compounds for the assigning of rotational structure to frequency is demonstrated by studies of polyvinyl chloride (PVC).¹²⁰ Four C—Cl stretching bands in the spectrum of PVC, namely $\alpha 14.49\mu$ (690 cm^{-1}), $\beta 15.67\mu$ (638 cm^{-1}), $\gamma 16.26\mu$ (615 cm^{-1}), and $\delta 16.58\mu$ (603 cm^{-1}) were found to be sensitive to the crystallinity, stereoregularity and configuration of the polymer chain.^{69, 86, 121} The assignments of the crystalline C—Cl bands 16.58μ (604 cm^{-1}), and 15.63μ (640 cm^{-1}) are completely consistent with a planar zig-zag syndiotactic structure. The noncrystalline bands are assigned based on the configuration of nearest neighbor Cl atoms. Adjacent Cl atoms are designated isotactic pairs or syndiotactic pairs, depending on whether the two Cl atoms are on the same side or on opposite sides of the polymer chain. In early studies of chlorine-containing molecules,⁸⁶ it was found that the secondary C—Cl frequencies depended on whether an H atom (S_H) or a C or Cl (S_X) was *trans* to the Cl atom. Later, it was found¹²¹ that this frequency depends on the nature of the substituent on both sides of the C—Cl bond as modes indicated by S_{HH} , S_{HC} , or S_{CC} . The S_{HH} notation is given to the C—Cl band of the extended syndiotactic structure, the S_{HC} notation to the folded syndiotactic structure, and S_{CC} to the isotactic threefold helix.

For a model consisting of two S pairs of C—Cl bonds, the rotational isomer possible can be described as follows: the planar zig-zag structure is most stable, and with it is associated an S_{HH} at 16.26μ (615 cm^{-1}).

The structure produced by rotating one end $+120^\circ$ about a C—C bond gives rise to an S_{HH} at 14.43μ (693 cm^{-1}). The structure (least possible) produced by rotating one end of the original zig-zag structure -120° about a C—C bond would give an S'_{HH} mode. For isotactic pairs, similar isomers are possible giving an S_{HH} at 685 cm^{-1} and (less stable) S'_{HH} at 15.67μ (638 cm^{-1}). An alternate interpretation of the two S_{CH} at 14.60μ (685 cm^{-1}) and 14.43μ (693 cm^{-1})¹¹⁹ is based on the probability of an isotactic threefold helix structure being present. The splitting of a fundamental into a parallel component 14.60μ (685 cm^{-1}) and a perpendicular component 14.43μ (693 cm^{-1}) would be in agreement with the observations. The former explanation seems more appropriate based on studies of heated PVC.¹²⁸ When PVC is heated,⁵⁵ the 15.67μ (638 cm^{-1}) band weakens markedly and the maximum of the 14.49μ (690 cm^{-1}) band shifts from 14.43μ (693 cm^{-1}) to 14.60μ (685 cm^{-1}). This is consistent with the expected isomeric changes with heating.

Normal Coordinate Analysis. Normal coordinate analysis of rotational isomers to assign frequencies may be used if model polymers and model analogs are not available. This technique will become more widely used with increase of computer programming of normal coordinate analysis.

It is not appropriate here to delve into the details of the method,¹³⁹ but its power is easily demonstrated. Normal coordinate analysis indicates the infrared bands in polyethylene glycol arise from a *trans-gauche-trans* chain structure.⁸⁴

The assigning of the absolute configuration by normal coordinate analysis from the changes observed in the spectra has occurred. Using propylene- $1d_1$ -*cis* and propylene- $1d_1$ -*trans* as monomers, the corresponding stereospecific diisotactic polymers were synthesized.⁸² The following scheme has been proposed by Natta for the formation of diisotactic structures:



Using the *threo* and *erythro* diisotactic structures as models, the infrared frequencies were calculated using an intramolecular potential previously defined. The calculated spectra were compared with the observed spectra. It was concluded that the propylene- $1d_1$ -*cis* double bond opened in a *cis* fashion to give a polymer with the *erythro* structure. Similarly, this opening of the double bond of the propylene- $1d_1$ -*trans* monomer resulted in the *threo* diisotactic structure. These examples compel one to be interested in the normal coordinate technique.

CONFORMATION OF THE POLYMER CHAIN

In the previous section, the effect of the configuration of a single repeat unit on the properties and spectrum of a polymer was examined. In this section, consideration will be given to sequences of structurally identical repeat units. When such sequences are present long range order results, and crystallization may occur. For some polymers, crystallization may induce changes in isomeric composition. These changes are termed conformational changes since they occur over the entire molecule, restricting it to a given structure. These conformational structures occur predominantly in the solid state, but they are also found in solution.

In 1949, Mochel and Hall,⁸⁸ in their infrared studies of the crystallization of neoprene, made the following comment:

"The surprising appearance of strong absorption bands when a polymer crystallizes are of interest because of their relation to order in the polymer."

They had discovered one of the most fascinating aspects of infrared spectroscopy — the detection of order in a polymer.

Band Types Characteristic of Transition to Crystalline-Ordered Polymer

Several characteristic types of infrared band changes reflect transition from amorphous or atactic to crystalline-ordered polymer. Krimm¹⁰⁵ has classified these changes into the following band types:

Type I. Bands which are weak or absent in the amorphous state and which increase significantly in intensity upon crystallization, in some cases also accompanied by slight frequency shifts. These bands can be of either dichroism, with no detectable separation of the components.

Type II. Bands which split into components having the same polarization upon crystallization. The frequency of separating the components increases with increasing crystallinity.

Type III. Bands which split into two components, one with parallel dichroism, and the other with perpendicular dichroism.

These characteristic band types are easily interpreted using the theory of ordered or helical polymers.⁵⁴

The Infinite, Single-Stranded Helix. For an infinite, single-stranded helix, coupling divides the total intensity of a normal vibration into a component parallel and perpendicular to the axis of the helix (Type III). If the coupling is very small, only one band will appear and its polarization depends on the angle of its transition moment with the helix axis (Type I). In an oriented sample, the two components, observed for strong coupling, define the absorption of plane polarized light perpendicular and parallel to the screw axis of the helical polymer chain, respectively, while the ratio of their absorbances determines the dichroism of the band. This ratio is obviously

dependent on the angle which the dipole moment of the normal mode makes with the axis of the helix. The ratio of the intensities (dichroic ratio) can be used to calculate the direction of polarization of the residue absorption relative to the helix axis.¹³⁰

$$I_{\perp} / I_{\parallel} = \tan^2 \theta \quad (8-4)$$

The intensities are measured from areas of plots of absorbance versus frequency and θ is the angle between the transition moment and the helix axis. Unfortunately, experimental difficulties prevent making these measurements⁶⁸ and usually the ratio of the absorptivities for plane polarized radiation incident and normal to an orientation direction are measured for a single band. It is very easy to identify the polarization properties of an infrared band for a partially oriented specimen. This knowledge is extremely useful for making band assignments.⁶⁸

The Infinite Isolated Helix. For an infinite isolated helix, the band splitting (the perpendicular component is doubly degenerate) is given by the following relations.¹³⁰

$$h(V_{\parallel} - V_0) = 2 \sum_{j=1} V_j, \quad (8-5)$$

$$h(V_{\perp} - V_0) = 2 \sum_{j=1} V_j \cos(2\pi j / P) \quad (8-6)$$

where

- V_{\parallel} = the frequency of component with parallel polarization,
- V_{\perp} = the frequency of component with perpendicular polarization,
- V_0 = the frequency of band with no coupling,
- V_j = the interaction with the j^{th} neighbor,
- P = number of residues per turn of the helix.

The parallel component is closest to the uncoupled frequency. The perpendicular band for the particular normal coordinate is shifted from the parallel component an additional amount, depending on the helix. This shift in frequency of the perpendicular component from the parallel component of a normal vibrational mode is the ingredient essential to an infrared spectroscopic comparison of the differences in the pitch of a helix. The shift in frequency is useful for determining the relative coiling of a helix but it cannot determine the absolute conformation or pitch of the helix since the interaction parameters are not known.

Detection of Helical Conformation

The presence of a helical conformation in the solution or solid state is characterized in the infrared by band splitting into components of opposite polarization (Type III bands). The number of repeat units required in the helical form to produce this splitting has not been determined. The infrared

spectrum (Figure 8-4) of the "smectic" state of polypropylene indicates the existence of coils, while the x-ray diagram is liquid-like. Annealing of the sample gives long range order and the x-ray diagram, as well as the infrared spectrum, reflects the helical conformation. The discrepancy between the x-ray and infrared spectra is a result of the sensitivity of the infrared to

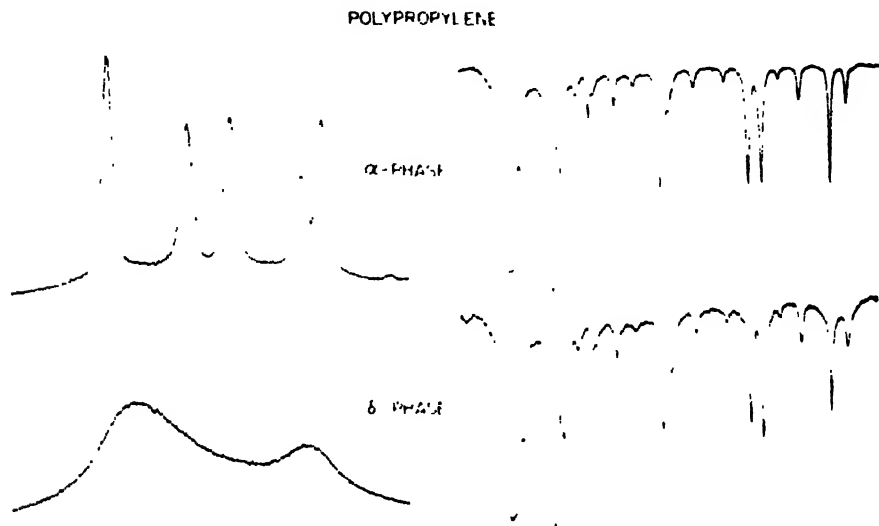


FIGURE 8-4. Infrared spectra and X-ray diffractometer scan of polypropylene.

short range order (smectic) while long range order (annealed) is required by x-rays. The infrared spectrum of synthetic polypeptides in solution indicates the presence of the α -helix, as shown in Table 8-1. For polypeptides, 5 monomer units are required to give the helical conformation as measured by infrared spectroscopy.

Changes in conformation are reflected by a frequency shift and or a change in the splitting of the parallel and perpendicular components. For polytetrafluoroethylene,⁹¹ the helical arrangement of 13 CF_2 groups in the identity period gives a CF_2 wagging mode at 15.7μ (635 cm^{-1}). At 19°C , the polytetrafluoroethylene helix unwinds to a helix containing 15 CF_2 groups in the identity period; this conformation gives a band at 16μ (625 cm^{-1}). For polybutene,²⁶ a solid state transition occurs where a helical identity unit containing nearly four monomer units changes into a helical identity unit containing 3 monomers; shifts in frequency and degree of splitting are observed in the infrared. Similar observations are made for the polyalkyl thioacrylates involving a non-threefold helix transforming to a threefold helix.

Coupling in the helical conformation changes the infrared spectrum dramatically. Theoretically, the coupling of units on adjacent helices has a similar effect, although, in practice, experimental evidence is not extensive. For strong coupling, three infrared bands are possible for each normal mode of the isolated residue in a double-strand helix like DNA: one polarized parallel and two perpendicular. The two perpendicular bands arise because the presence of another coil creates an asymmetry of the force field compared to a single strand helix.

For the infinite double-stranded helix,⁶ the three bands of a particular normal mode are located by the following:

$$h(V_{||} - V_0) = V + 2 \sum_{j=1} (V_j + V'_j), \quad (8-7)$$

$$h(V_{\perp} - V_0) = V + 2 \sum_{j=1} (V_j + V'_j) \cos(2\pi j P), \quad (8-8)$$

$$h(V_{\perp} - V_0) = V + 2 \sum_{j=1} (V_j - V'_j) \cos(2\pi j P), \quad (8-9)$$

where

V_0 = the interaction between nearest neighbors on opposite strands,

V'_j = the interaction between j^{th} neighbors in Chain 1,

V_j = the interaction between j^{th} neighbors in Chain 2.

The relative intensity of the two perpendicular bands depends on the relative orientation of the vibrating groups of the opposite strands

$$I_{\perp} / I_{\parallel} = \tan^2(1/2\gamma') \quad (8-10)$$

where γ' is the angle between the perpendicular components of the polarization directions of absorbing groups. Unfortunately, no experimental evidence is available to check these theoretical predictions. This may be due simply to the small perturbation of such coupling of the spectra.

Formation of an infinite triple-stranded helix should give a spectrum of a single normal mode with three perpendicular bands and two parallel bands. No such spectrum has yet been observed.

The prime example of a Type II band is the 9.34μ (1070 cm^{-1}) band in polystyrene.¹⁰³ The band is found at 9.41μ (1063 cm^{-1}) for molten atactic polystyrene. A quenched low crystallinity polystyrene has a band with two perpendicular components: one at 9.27μ (1078 cm^{-1}) and the other at 9.434μ (1060 cm^{-1}). Annealed highly crystalline polystyrene gives the perpendicular components at 9.242μ (1082 cm^{-1}) and 9.514μ (1051 cm^{-1}). Krimm¹⁰⁴ interprets the observed splittings as being related to degrees of departure from extended threefold helical symmetry. This would account for the splitting of the normally degenerate perpendicular component. The conformation disorder is introduced by the rotation of the benzene ring about the bond connecting it to the chain.

Polypeptide Chains

It has been recognized that polypeptide chains may exist in extended conformations as well as folded helical conformations. In the fully extended conformation of polypeptides, interchain hydrogen bonds may be formed satisfactorily only when the polypeptide chains are antiparallel. However, in this conformation steric factors between β -carbons of adjacent chains is appreciable. Thus, polypeptide chains tend to exist in more or less buckled conformations as either the parallel-chain pleated sheet or the antiparallel-chain pleated sheet. These two extended conformations as well as the random coil and helix are easily detected in the infrared⁸⁴ as shown in Table 8-1.

TABLE 8-1.

Conformation	Designation	Amide I Band	Amide II Band
Random coil	V_0	6.039μ (1656 cm^{-1})	6.515μ (1535 cm^{-1})
α -helix	V_{II}	6.061μ (1650 cm^{-1})	6.596μ (1516 cm^{-1})
	V_{II}	6.053μ (1652 cm^{-1})	6.468μ (1546 cm^{-1})
Parallel-chain	V_I	6.079μ (1645 cm^{-1})	6.536μ (1530 cm^{-1})
Pleated sheet	V_{II}	6.134μ (1630 cm^{-1})	6.452μ (1550 cm^{-1})
Antiparallel-chain	V_{II}	5.935μ (1685 cm^{-1})	6.536μ (1530 cm^{-1})
	V_{II}	6.127μ (1632 cm^{-1})	...
	V_{II}

Conformational Changes in Polycaprolactam

For crystalline polymeric systems, differences in conformation resulting from different crystalline unit cells are reflected in the infrared region of the spectrum. The nylon polymers exhibit several different conformational forms.²⁰ The amide-amide association is the main factor controlling the conformation and packing of the chain in the ordered and disordered structures.

In studies²² of injection molded pieces of polycaprolactam at 20°C (high supercooling), the x-ray pattern shows an amorphous structure almost identical to the polycaprolactam melt. However, infrared spectroscopy demonstrates an essential difference in order. The free N-H band at 2.9μ (3448 cm^{-1}) in the quenched amorphous state shows only a few hydrogen bridges exist, whereas in the melt almost all possible hydrogen bridges are saturated [no 2.9μ (3448 cm^{-1}) band]. With increasing temperature (30° to 150°C), there occurs a transformation to a hexagonally ordered phase which may be followed by the increase in absorption of the 10.25μ (975 cm^{-1}) band. This transition occurs from frozen-in amorphous phase to a state of order which may be regarded as a parallelization of molecular chains, and pseudocrystallinity, as indicated by the appearance of a peak superposed

on the amorphous halo in the diffraction pattern. With increasing temperature, this hexagonally ordered phase increases at the expense of the amorphous phase and, at about 180°C, reaches its maximum concentration without the amorphous structure disappearing completely, however. From 180°C, the crystalline monoclinic structure is formed from the hexagonally ordered structure as characterized by two different types of lattice spacings indicating three dimensional ordering in the diffraction pattern and crystalline absorptions at 9.75μ (1026 cm^{-1}), 10.45μ (957 cm^{-1}), 10.7μ (935 cm^{-1}), 12.0μ (833 cm^{-1}), 13.8μ (725 cm^{-1}) and 14.5μ (690 cm^{-1}) in the infrared regions. Upon approaching the melting point, the hexagonal phase vanishes. It is thus possible, by coupling x-ray, thermal, and infrared studies, to ascertain the nature of the conformational changes in a system as complicated as polycaprolactam.

Spectroscopic Methods for Crystallinity Determination

The absorption spectrum of a partially crystalline polymer can be considered as a superposition of the spectra of amorphous and crystalline domains. The detection of "crystalline" and "amorphous" absorption bands is possible from investigations of infrared bands, as a function of temperature, density, and thermal history.⁴⁸ In conjunction with x-ray investigations,^{118,131} the correlation of absorption bands with possible crystalline and noncrystalline molecular modifications can be made. Using these characteristic bands, spectroscopic methods for the determination of crystallinity appear to be valid. The spectroscopic crystallinity determination is based on the assumption that the extinction ϵ_c of a crystalline band is proportional to the volume fraction (X) of the crystalline component and the extinction of a noncrystalline absorption ϵ_A is proportional to the volume fraction noncrystalline component ($1 - X$),

$$\epsilon_c = K X, \quad (8-11)$$

$$\epsilon_A = A(1 - X) \quad (8-12)$$

where A and K are the respective constants of proportionality. It is possible to determine the proportionality constant by assuming a linear relationship between crystallinity and density.¹²⁵ For simple systems without additional components being present due to isomorphic molecular arrangements, this density technique for calibration is useful and has been applied to polytetrafluoroethylene,¹³⁰ polychloroprene,⁹⁰ polyethylene,²¹ polyethylene terephthalate,²³ and polystyrene.⁶⁰

When more than one component is present, the density method of calibration is valid only in certain cases. For example, for polycaprolactam, density changes in the range 1.10 to 1.132 g/cm³ are to be traced to modifications occurring within the noncrystalline phases.⁵³ Another

method^{49,52,132} is used to account for changes in molecular order. By elimination of X from the above equations, one obtains

$$\epsilon_d = A[1 - \epsilon_c/K] \quad (8-13)$$

Dividing by ϵ_c gives

$$D = \frac{\epsilon_d}{\epsilon_c} = A \left[\frac{1}{\epsilon_c} - \frac{1}{K} \right] \quad (8-14)$$

If these considerations are valid, a plot of ϵ_d/ϵ_c versus $1/\epsilon_c$ should yield A and K . The crystallinity is obtained from the equation

$$X = \frac{1}{D \frac{K}{A} - 1} \times 100 \quad (\%), \quad (8-15)$$

involving the measured quantities ϵ_d/ϵ_c , and should be independent of density and layer thickness of the sample involved. This method resolves itself into the determination of the absorptivities of two independent absorptions. It has been applied primarily to the nylon series of polymers.⁵²

In some polymers, separate bands characteristic of the ordered and disordered phases cannot be found; cellulose³³ and polyhydroxymethylene¹⁷ are polymers of this type. For these two examples, spectroscopic methods have been developed that create new bands for the disordered regions based on the experimental observation that D₂O will only hydrogen-bond and diffuse in the disordered regions of the polymer. Thus, the amorphous content is proportional to the intensity of the O—D str band at 3.952 μ (2530 cm⁻¹) and the crystalline content is proportional to the residual O—H str band at 2.976 μ (3360 cm⁻¹).¹⁰⁷ This measurement is an excellent method for comparing the relative order in cellulose samples, but later work has revealed that deuteration of the crystalline regions occurs with time,⁵⁹ or higher temperatures,¹⁰⁴ or elastic deformation¹¹⁰.

Orientation and Polarized Radiation

In addition to the conformational or structural factor, there is also an orientation effect in the intensity of infrared absorptions which is useful in detecting changes in the conformation of a polymer chain during the process of working or drawing. The intensity of an infrared band is dependent upon the orientation of the electric vector of the incident radiation with respect to the absorbing transition moment. Consider a segment of a polymer chain, for example, an ester group. For the carbonyl str vibration, the dipole moment change is along the carbon-oxygen bond axis. If one individual carbonyl group could be analyzed with plane polarized radiation, a strong absorption band would be observed when the electric vector of the incident light is parallel to the carbonyl bond. Radiation with the electric

vector perpendicular to this bond would not be absorbed. An actual polymer sample may contain many carbonyl transition moments oriented in various directions. The absorption intensity in any given direction is determined by the super-position of the contributions from each individual carbonyl group. Hence, as the carbonyl groups are aligned in a given direction (by aligning the polymer chains), the intensity of light polarized along this direction will increase. This increase in intensity can be used to measure the amount of orientation in a given sample.

If the angle between the dipole moment for the normal mode and the direction of polarization of the incident electric vector is θ , the extinction for each group is $\epsilon \cos^2 \theta$ where ϵ is the extinction coefficient per group for light polarized along the direction of the dipole moment. The function representing the fraction of N molecules lying between θ and $\theta + d\theta$ is

$$dN = f(\theta) d\theta, \quad N = \int_0^\pi f(\theta) d\theta. \quad (8-16)$$

Unfortunately, the precise nature of the orientation distribution function $f(\theta)$ cannot be determined explicitly. Hence, to date, only qualitative interpretations of the studies using polarized infrared light have been made.^{34,45}

CONCLUSIONS

The role infrared spectroscopy plays in the research and development of polymers is an important one. The initial characterization of the polymerization product and byproducts, the isolation and identification of the major components of the chain structure, the semiquantitative determination of stereoregularity, crystallinity, copolymer composition, sequence distribution, branches, and end groups, and finally, quality control methods for processing have all received the attention of infrared spectroscopists in the support of polymer research ventures. Special techniques have been developed for specific polymer problems including attenuated total reflectance, polarization, and compensation.

The future role of infrared spectroscopy in polymer research should be even more fruitful. Improved infrared effectiveness will result from the increasing availability of grating instruments for high resolution studies, far infrared instruments for wider range, digital techniques for band contour and intensity measurements, and computer programs for normal coordinate analysis procedures.

The use of infrared spectroscopy in conjunction with other techniques such as x-ray diffraction, Nuclear Magnetic Resonance (NMR), and optical rotatory dispersion in the studies of polymers will continue to increase since each technique plays a specific role in polymer structure elucidation. The

difference in sensitivity with respect to order in polymers is just one example which illustrates the contribution of each technique to a broader understanding of the polymer. X-ray diffraction stands alone in its elegance with respect to long-range three dimensional order, as illustrated by the monoclinic crystalline form of polypropylene, while NMR is elegantly sensitive to local bond environment, as illustrated by its sensitivity to the stereoregularity of polypropylene. Infrared measurements are sensitive in the intermediate range, as illustrated by studies of the "smectic" form of polypropylene. The joint efforts of all of these techniques are essential to gain a thorough knowledge of a polymer system.

New vistas will open for polymer analyses when new and powerful sources for Raman spectroscopy are developed. A Raman spectrometer employing a Laser source is now available commercially. Vibrational modes important for configurational and conformational studies often are weak or inactive in the infrared; these bands are strong in the Raman effect. For many polymers, bands inactive in infrared are active in Raman and vice versa. To date, only a few polymers have benefited from Raman analysis. Raman data are essential to refinement of normal coordinate analysis procedures.

Improved polarization devices and techniques will make orientation studies more meaningful. The imperfect polarization and instrumental distortion nullify this potentially powerful tool for polymer studies. Tilting experiments (three dimensional orientation) will be extremely valuable in defining orientational effects.

Finally, the infrared spectroscopist is only as powerful as his knowledge of polymers. The spectrum does not telecast the structure, configuration and conformation of the polymer; the spectrum must be interpreted in terms of sound polymer physics and chemistry, and a thorough knowledge of infrared principles. Continued improvement in both of these areas will be reflected in sound, useful infrared spectroscopy of polymers.

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CHAPTER

9

Infrared Analysis of Essential Oils, Related Products, and Cosmetics

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INTRODUCTION

This chapter will discuss the application of infrared absorption techniques, mainly to essential oils and related products, and to a lesser extent to cosmetics. Related products are essential oil isolates and synthetic compounds which are called "aromatics" because they have an aroma. While essential oils and aromatic chemicals lend themselves to direct sampling methods, extensive use of infrared in the cosmetic field has been somewhat discouraged due to sampling difficulties, since water, inorganics, and non-transmitting materials are involved. Essential oils and aromatic chemicals are basic raw materials for cosmetic preparation, therefore requiring the cosmetic chemist's knowledge of these.

Some discussion on the types of products, their sources, methods of production, chemistry, background, problems, and the nature of the industry will tend to orient the newer instrumentalist and prepare him to properly apply his infrared techniques. The above products are widely used by many people and industries for scenting and flavoring all kinds of finished products from the mixing of the most expensive perfumes to the basic necessity of flavoring foods in remote sections of the world.

Types of Products Considered

Essential Oils. Essential oils are volatile natural products responsible for the essence or odor of plants, and, in a few cases, desirable animal or fossil products. There are various methods of producing these oils from natural

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products, the most common being steam and water distillations. Plant parts are distilled to yield a variety of possible oils. Thus rose or ylang-ylang flowers or blossoms yield distilled oils, as do pimenta berries, lime fruit, clove leaves, clove stems, clove buds, rose wood, cinnamon bark, ginger root, and turpentine gum. Heat sensitive flowers, as tuberose and jasmin, are extracted cold with a high purity fat. Plant parts are also extracted with various other solvents yielding correspondingly different products, such as oleoresins and resinoids which contain the essential oil plus nonvolatile extractives. These products can be steam or water distilled to yield a volatile oil, sometimes differing because of the original extracting solvent. Plant gums or exudates are also of interest in this chapter. Some will yield volatile oils. A large volume of citrus fruits are hand or machine pressed for their water insoluble volatile oils; these include orange, lemon, grapefruit, bergamot, limes, mandarin, tangerine, bitter orange, etc.

Related Products. Related products include isolates and synthetics. In many natural products a certain component, or group of components, is of particular interest since it is the main odor principle. Such things include citral (3 to 5% in lemon oil), eugenol in clove oil (60 to 90% depending on the plant part), cinnamic aldehyde (70% in Cassia oil), *l*-carvone (70% in Spearmint oil), *d*-carvone (50 to 60% in caraway oil) rhodinol (a mixture of geraniol, nerol and citronellol isomers about 30 to 40% in Geranium oil), and piperine (an amide found in black pepper). Such products are concentrated or purified by vacuum distillation or chemical separations. Some can be synthesized totally by starting with natural intermediates. Cedrol is isolated from cedarwood oil and acetylated to produce cedryl acetate, a valuable perfume ingredient with a desirable woody note. Linalool is rectified out of rose wood (Bois de Rose) and acetylated to make a chemical which is the main odor principle of lavender flowers. For many years eugenol was isolated from clove oil as the alkali phenolate, converted to isoeugenol, and oxidized to vanillin, the main flavor component of vanilla. Large quantities of this material are now produced from lignin, a by-product of the paper and wood pulp industries.

Imitation Oils. Imitation oils are compounded to replace in part very expensive or rarely produced oils. Greater knowledge of chemical constitution aids in better duplication of the natural product. It is often necessary to make component substitutions of readily available homologues, isomers, or similar components for rare, difficult-to-synthesize organics. These alter the odor or chemical and physical characteristics sufficient for determination.

Cosmetics. Cosmetics include a variety of scented products, perfumes, colognes, toilet waters, soaps, powders, lipsticks, creams, depilatories, hair

preparations, lotions, suntan preparations, etc. These products contain inorganic compounds, water, alcohols, solubilizers and other solvents in solutions, emulsions, creams, etc. They can rarely be subjected to infrared analysis as such, but require prior chemical or mechanical separations.

Chemistry of Products

The chemistry of essential oils is a field all its own. Many notable chemists have spent their life's work within its bounds. The work on terpenes and sesquiterpenes, elucidation of structures and reactions has held, and will continue to hold, the interest of many chemists throughout the world and to test their resources. What is said concerning the chemistry of essential oils applies as well to essential-oil isolates and to synthetics, but to a lesser extent, because they are less complex. Essential oils are mixtures of organic chemicals varying over a wide range in type, number of components, and concentrations. Fifty components in an individual oil are not uncommon. Some components have such powerful odors that variations in the order of 0.1% change the odor considerably, e.g., dimethyl sulfide in crude and rectified peppermint and spearmint oils. The chemical components include hydrocarbons with many degrees of saturation, aromatic rings with many group and positional substitutions, aldehydes and ketones, alcohols, esters and lactones, ethers, amides, amines, acids, and some sulfur compounds. Often in the absence of their natural plant antioxidants, or when placed in a different chemical environment such as change in pH or exposure to air or heat, these chemicals will isomerize, dehydrate, polymerize, or react. In certain cases such sensitivity has made wet chemical separations, and even mechanical separations, difficult. The lack of component identification has somewhat hindered the quality standards of these products. It is obvious that one cannot assay for a component whose structure or functional groups are vague.

Classical Analytical Methods

Methods Used and Their Disadvantages. Because of their lack of specificity, the older so called wet methods of analysis are not always adequate. Essential-oil wet analysis includes specific gravity, refractive index, optical rotation, acid value, ester value, ester value after acetylation (for alcohols), phenol determination, solubility, etc. Ester value⁴ does not differentiate alcohol or acid component, except that calculations are made according to the molecular weight of the most prominent ester. Refractive index and optical rotation are additive factors and of limited specific value. A total menthol specification on peppermint oils is misleading, for what is computed as menthol by saponification of the esters of the oil after acetylation includes

menthol isomers, other alcohols, or any enols of ketones and aldehydes which may acetylate.

Accomplishments of Classical Techniques. In spite of these drawbacks, many authentic samples have been collected, subjected to wet analysis, and specification constants set up. Coupled with accurate and practiced odor evaluation, good quality control can often be maintained. Few, however, have the availability of authentic samples or the skill of odor evaluation. For those that have, the natural uniformity and odor of the individual oil has enabled the essential oil chemist not only to classify the plant origin, but sometimes to describe its place of growth, or even to infer its human origin. The vast amount of work done by such men as Gildermeister, Hoffman, Wallach, Tiemann, Semmler, Tilden, and Kleber, to mention a few, can never be overestimated. They recognized and overcame many physical and chemical obstacles to classify and describe the components of so many authentic oils. Many of these analyses have not been improved upon to the present day. To have put modern instrumental techniques into the hands of these imaginative and tireless workers is sure to equilibrate the pride the modern workers take in their startling discoveries; but in spite of their technical improvements and the physical, chemical, and odor constants they have established, adulterations within specifications have become increasingly possible due to the recent expansion of the synthetic chemical industry. Infrared spectrophotometry has again swung the balance toward the quality minded chemist. -

NATURE OF THE INDUSTRY

It is proper to mention here some of the characteristics peculiar to the industry. It is the nature of an industry, where expensive products are handled which are so concerned with and appealing to human sensation, that adulteration or sophistication may take place. These terms are used to describe the dilution, for profit, of a pure expensive oil or product with a less expensive substance. Adulteration is the use of a cheap chemical substitute; sophistication is the use of the same chemical but of less expensive source. Both are attempts to defraud and can be skillfully accomplished to avoid detection.

Other characteristics of the industry, brought about by keen competition, are the paucity of patents, the secrecy of processing and analytical methods, and the lack of scientific publications in spite of the large volume of work in all fields. Also, there is a certain resistance to modern scientific methods, for it is an industry where art and rare skills still defy definition. The incomplete knowledge of products and inadequacy of analytical methods spread a mysterious shroud over its exotic products. Only well proven, time

honored methods are accepted from the outside. Is it any wonder, therefore, that a beam of light, namely infrared, has changed the view of the entire industry.

UTILIZATION OF INFRARED IN THE INDUSTRY

In 1896, some of the first samples subjected to the crude infrared instrumentation of the day, by Donath, were several essential oils. These early experiments were forgotten.

Advantages

The infrared method was almost custom-built for the essential oil industry. The ability to identify components of mixtures, which is the forte of the infrared method, has always been the weak point in essential oil science. Although slow to accept this method, great progress has been made throughout the world in the last decade, but again typical of the industry, very little has been published.

The advantages of infrared absorption methods, which have been emphasized by reported results in other fields, also apply to essential oils, related products, and cosmetics. Many emphasize speed of analysis. This is not always true. What it does for this industry is to make known many things which were formerly neglected. There is so much information to be obtained from a single infrared spectrum that proper evaluation is time consuming. Once the routine has been established, then may rapid analyses be accomplished. The semiquantitative nature of normal run in the same cell is an important help in establishing component ratios. These relative component concentrations have been used by Levi⁴ to establish the authenticity and adulteration of ylang-ylang oils. It is normally the trace or low-concentration components which indicate processing method or treatment of a product. The proportional disappearance of these trace components indicates dilution. Variations in the ratios sometimes indicate natural variations, harvesting time, climate, rainfall, age of plant material before distillation or processing. These aspects will be discussed later in this chapter.

Another advantage of the infrared method, so apparent in the steroid field, applies also to essential oil-products, namely, that the sample is unaffected by analysis. Wherever sensitive chemicals are involved, this circumstance cannot be overlooked.

When chemical reactions are required to separate a component, a quick look at the infrared spectrum can confirm that the component has been unchanged in isolation. The reproducibility of modern infrared instrumentation has made functional group quantitative analysis specific and accurate.

The infrared method in essential-oil chemistry has assumed its true place between those who still insist it has little value, and those who claim it has all the answers.

Weaknesses

It is not proper to mention all of infrared's advantages and none of its weak spots. Its main weakness is insensitivity to certain trace components which may have very strong odors. Compared to the human nose which can detect some substances in ~ 10 to 12 molar per cent concentration, infrared detectors and systems are no match; such things as fatty aldehyde, or alcohols are examples. However, there are cases of other substances such as diethyl phthalate, nitro musks, coumarin, etc. which have low odor-sensitivity or are overpowering, where the instrument is many times more accurate in fixing or detecting concentration than the nose.

Techniques

Liquid Samples. Infrared analysis of products in this industry utilizes all techniques which can be applied to any organic chemicals. Since most essential oils, isolates, and aromatics are liquids, normal runs are in fixed thickness cells generally in the 25 to 30μ path length range. Some aromatics, such as methyl salicylate or phthalates, absorb so strongly in certain regions a sandwich, demountable, or capillary cell is used with sample thickness in the 5 to 15μ range. Spacers may be used to insure comparative thickness for semiquantitative runs, but in purely qualitative runs no spacer is necessary.

As the sample is diluted with an infrared solvent, the thickness of fixed cells may be used to emphasize the peaks of interest. Many essential oil spectroscopists consistently run their samples as 10% solutions in CS_2 and/or CCl_4 in a 100 or 200μ cell. The resulting curves, when cell thicknesses are accurately calibrated, are in effect quantitative in nature (see Chapter 6). This procedure is recommended for certain oils and many aromatics, but for complex essential oils, peak interference negates the specific quantitative nature of the analysis.

Solid Samples. Only a few essential oils are solids, e.g., Oil of Guaiacwood. Many oleoresins are semisolid. Some isolates and synthetics are solids. It is best to run solids in solution whenever possible.

For samples that melt below 90°C , good results can be obtained by placing the whole cell assembly in an oven with a few crystals of the solid on the upper face of the salt plate set in the holder. When the crystals melt, the other heated salt plate may be placed on top and the cell assembled. Often the pressure on the plates and the heat of the instrument will prevent recrystallization. If crystallization takes place, the film of crystals will, in most cases, transmit well enough to give a good solid state spectrum. The

varying changes in spectrum, due to state of sample, must be expected here. It is often difficult to correlate solid and liquid or solution samples, especially when hydrogen bonding effects may be encountered, as with acids and esters.

The use of mulls or finely ground samples in an infrared transmitting carrier is adequately explained in Chapters 4 and 6. A small mortar and pestle or an electric vibrator may be used to reduce the crystal particle size sufficiently. It is well, when mulls are first run, to run a curve of the carrier, Nujol, or fluorocarbon, treated in the manner the sample will be ground. Since silicon-oxygen bonds have extremely strong infrared bands, finely powdered parts of the grinding apparatus are sometimes found in the carrier. It is necessary to recognize these interfering peaks for proper mull identification. The best way to run *Oleoresin Black Pepper*, which is a nonhomogeneous mixture of a fixed fatty oil, an essential oil, and a solid amide insoluble in the oils, is to grind it to reduce the amide crystals, allowing the fatty oil to act as a carrier. Certain amorphous materials, gums, resin acids, and sugars (mainly water soluble materials) are difficult to mull because they lack actual crystalline structures. They tend to cake and cannot be made to disperse evenly. Grinding in a mixture of low-boiling polar solvent, such as ethyl ether, and a fixed oil, such as Nujol, may suspend fine particles of the solid in the Nujol as the ether evaporates.

KBr and KCl pellets are sometimes used in this field, but this method is recommended when difficulties in solution, mull, or melted film occur.

Prescan Sample Treatment. It is obvious that as the number of components in a given sample decreases, the accuracy and completion of infrared functional and structural analyses increase. Sample preparation plays an extremely important part, therefore, in infrared techniques. The modern infrared spectrophotometer, no matter what its design characteristics are, cannot improve on the sample that is presented to it. The sample examined should be treated mechanically or chemically to remove unwanted interferences as much as possible. The bands of the compound of interest must be allowed emphasis. It is well, therefore, to have available certain laboratory equipment and facilities that will permit fractionation or vacuum distillation, column, paper and vapor phase preparative chromatography, chemical separations, e.g., Girard's reagent for aldehyde fixation (borate fixation of primary or secondary alcohols (which can be regenerated with water), and differential solubility equipment which runs from separatory funnels to counter-current liquid-liquid columns. All these things increase the performance of the instrument much more than certain tedious instrument calibrations.

Sample Peculiarities. Mention should be made here of certain problems which are peculiar to the samples of this industry. Being in most cases steam

distilled, and in many cases known to contain hydrophylic components such as alcohols and esters, essential oils and certain isolates often contain water. Oil of Bois de Rose, containing 85% linalool, is very difficult to dry. It is impossible to dry it using inert anhydrous salt driers, such as magnesium sulfate or sodium sulfate. Three or four per cent water is not uncommon. Unless this can be reduced to trace amounts, accurate infrared spectra of Bois de Rose oils cannot be obtained. A simple test for water is to add about 5 drops of carbon disulfide or carbon tetrachloride to an equal amount of the oil. A hazy or cloudy solution indicates water. Disregarding the very strong absorption of water, which invalidates the spectrum, its effect on cell service is pronounced. Phenyl ethyl alcohol can hold 8% water without clouding or separating. When anhydrous salts lack facility, subjecting the sample to a vacuum with little or no heat will dry the sample unless very volatile compounds are involved.

Another hazard, which is confusing when first encountered, is the appearance of the extremely strong silicone peaks when the sample is mechanically or chemically treated in ground glass equipment where greases are used on joints, stopcocks, etc. Antifoam compounds also appear in the distillation residue or extract; once seen, however, they are easy to recognize but difficult to remove.

Reference Chemicals. The previously mentioned laboratory facilities can also be used to produce reference compounds of known purity. It is necessary for any essential-oil laboratory or any instrumental laboratory to have a library of pure reference chemicals. Many spectra services are available, but few offer the hundreds of special compounds required by this industry. There is no substitute for a sample isolated or synthesized under one's own supervision. In this regard, the availability or cooperation with a synthesis research laboratory is helpful; their skill can guarantee a pure product. Where a factory or plant is in existence, it is very advantageous, when a pure compound is desired, to take a sample of a "heart cut" or "center cut" in a large scale or production distillation. The purification of this already pure material is much simpler and larger samples are available. The use of factory separations or fractions permits identification of trace components. Therefore, plant facilities will also produce authentic samples of steam-distilled oils so necessary for reference compounds. Often work in this industry is based on samples of doubtful origin.

Sample History. Another important aid to a spectroscopist in this field is the complete background or case history of the sample to be analyzed. Such things as method of production, where produced, and by whom, should be determined. A complete wet chemical analysis has often solved a difficult problem. Such simple things as color give a necessary lead to an intelligent spectroscopist, disclosing for instance, by a green color, that a

labdanum or lavender concentrate was used in a perfume formulation. A good nose saves much time, for with practice the most sensitive sense of smell can often classify an unknown compound and direct the investigation through certain chemical types.

Procedures in the Industry. While on the subject of techniques, those which have been applied in this industry may be briefly discussed. In addition to the normal range of fixed-thickness cells from 25 to 1000 μ , it is well to have several sets of matched cells for differential work. In spite of the fact that interpretation of differential curves of complex compounds must be cautiously considered, their usefulness on simpler mixtures makes them a necessary addition. Variable thickness cells are expensive, of very limited use, and are difficult to clean without fogging.

The use of acetone as a cleaning solvent produces no problems. Some recommend hexane, since the presence of slight amounts in an incompletely dried cell does not alter the spectrum to any degree. However, not all essential-oil components are as soluble in hexane as they are in acetone. The chlorinated solvents also lack solvent power and have extremely strong bands as well. Acetone is recommended for general cleaning. Drying is accomplished by pulling dry air through the cell with a vacuum pump.

Microcells have come into extensive use since the advent of vapor phase chromatography (VPC) instruments and sample collection apparatus. These cells require special attention. No specific techniques are recommended; necessity will dictate them. Soon the spectroscopist will be attempting to modify the cell to take smaller and smaller volume.

Although normal fixed thickness cell runs are semiquantitative in nature, certain techniques are to be followed in doing quantitative analyses. These are amply explained in an article written by the Essential Oil Association for *Applied Spectroscopy*.¹ Scale expansion has become an important instrumental specification. Microcell techniques often demand this. The use of transmission filters or screens, wide slits, and high energy sources have their applications to certain samples. Their qualities and drawbacks are explained in Chapter 3.

APPLICATIONS OF INFRARED

With the foregoing description of basic sample and instrument information, specific for this industry, applications of infrared are now discussed.

Quality Control

Prime Oils. Although mentioned previously, the necessity of authentic samples cannot be overemphasized. The procurement of authentic samples involves rugged journeys to the production source, collecting the sample

right from the field process, and processing by normal methods a carefully selected raw material, herb, etc. These are called prime oils. Many seasonal and climatic variations are involved. The prime oil is given a special acceptability by perfumers, the flavor chemist, and the essential-oil chemist, who then dictate such things as plant maturity, processing method, and time to reproduce this desirable product.

Climatic and Seasonal Variations. Climatic variations are responsible for oils of different chemical composition. Such is the case of Geranium oil which is produced in several localities. The oil produced on Reunion Island is known as Bourbon geranium oil and is preferred by many perfumers over the oil produced in Algeria or Morocco, which is usually in greater supply. There are certain subtle differences in the infrared curves of the two types. In the 8.5μ region, the strong band is due to formates. Here the Reunion oil is slightly lower than the Algerian (confirmed by wet analysis). Chemical analysis also indicates that there is more total alcohol in the Algerian type. This is shown on the infrared curve at 2.9 to 3.0μ where hydroxyl groups absorb. A third type of geranium oil, known as Mawah or East African geranium oil is considered a less desirable oil and is not produced to any great extent. It can be distinguished by low formate content (8.5μ) and a higher sesquiterpene content, showing stronger bands at 11.3μ than the other oils.

Nutmeg oils also show differences in composition, the East and West Indian types easily differentiated by infrared (Figures 9-1 and 9-2). The West Indian oil is very terpeney, showing stronger bands at 11.3 to 11.6μ . The East Indian oil contains more oxygenated materials, some of which are strong infrared absorbers such as Eugenol and saffrole. The oxygenated substances are responsible for the differences at 8.9 and 9.6μ . Part of the

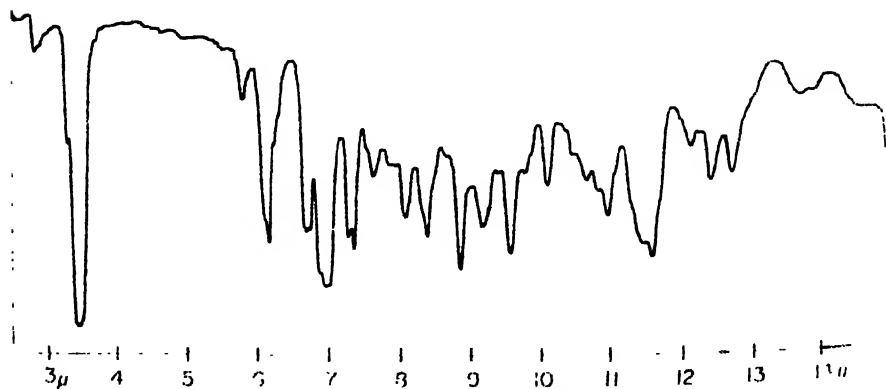


FIGURE 9-1. Oil of nutmeg, East Indian.

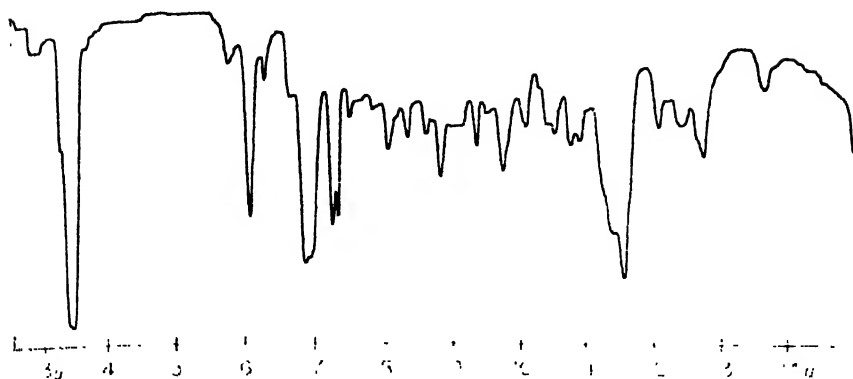


FIGURE 9-2. Oil of nutmeg, West Indian.

variation between the two types is probably due to a variation in the method of producing the two oils. The East Indian fruit is picked from the tree before the husk splits; the West Indian fruit is picked from the ground where it has fallen after the husk splits.

Production Method Variations. Different production methods are responsible for variations in an essential oil derived from a botanical in different ways. Such is the case with lemon oils, where, although slight botanical differences do exist, several types of oil are available because of differences in processing. Handpressed oils from Italy are produced by removing the oil from the peel in the absence of the juice (Figure 9-3). Cold pressed oils from California are produced as a by-product in the production of juice by centrifuging the juice-oil mixture to separate the two (Figure 9-4).

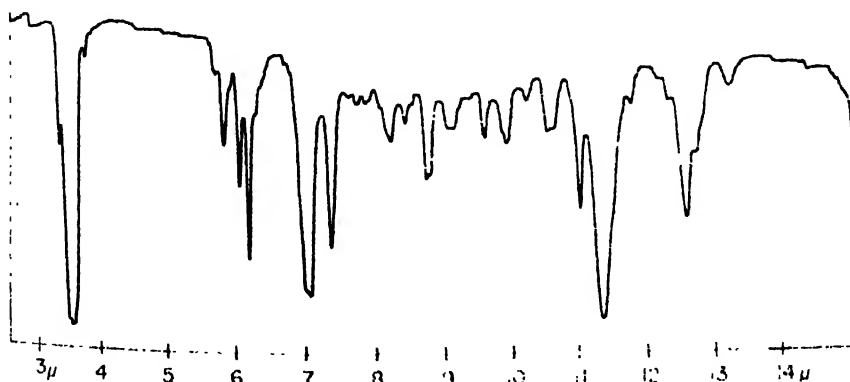


FIGURE 9-3. Oil of Lemon, Italian.

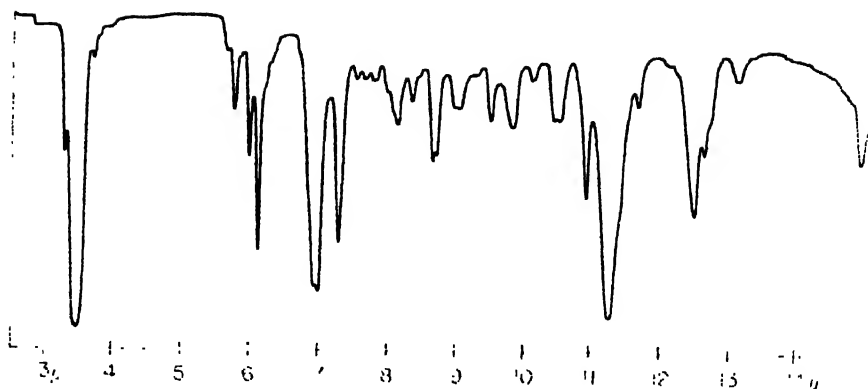


FIGURE 9-4. Oil of lemon, California cold pressed.

The infrared spectra differ since water soluble components are not removed from the handpressed oil by contact with the juice, as they are in the California oil. Infrared differences can be seen at 5.98μ (citral) and 12.15μ (coumarin homologs).

A third type, so called distilled oil, is produced by steam distilling the juice-pulp mixture and is lower in oxygenated components such as citral, alcohols, coumarins, and esters.

It is a general procedure with lemon, as with many oils, to produce concentrates by removing hydrocarbons which do little for the flavor but hasten spoilage. These concentrates are available as terpeneless, sesquiterpeneless, or concentrated oils of varying strength of flavor such as five fold, ten fold, etc. It is possible to evaluate these concentrates by examining the infrared curves for the proper ratio of aldehydes, esters, and alcohols to the decrease in terpenes. As an oil is concentrated, the citral increases and the acetates, such as geranyl acetate, become more apparent. If a distilled oil has been concentrated, the coumarins do not increase proportionately, while a handpressed or coldpressed oil will show this difference.

If concentration is accomplished by vacuum distillation, the lower boiling terpenes will be removed first. This is observable at 12.7μ , for example, when alpha-pinene decreases before the other terpenes. The ratio of the bands at 12.8μ (shoulder) due to gamma-terpinene and 12.3μ due to *para*-cymene indicates the amount of spoilage which has occurred. Since the terpinene oxidizes to *para*-cymene in the initial spoilage reaction, an increase in *para*-cymene and a decrease in gamma-terpinene is indicative of the degree of spoilage which has taken place. It should be mentioned, however, that even a fresh oil of the best quality does contain a limited amount of *para*-cymene.

Component ratios also play a role in the evaluation of rose oils which are produced by two methods. The extracted oil (Figure 9-5) (extracted mainly with petroleum ether) is rich in phenyl ethanol, while the distilled oil (Figure 9-6) is very low in this water soluble alcohol. While both oils show equally strong bands at 3μ , due to the hydroxyl components, the distilled oil contains very little phenyl ethanol as seen by the lack of bands at 13.4 and

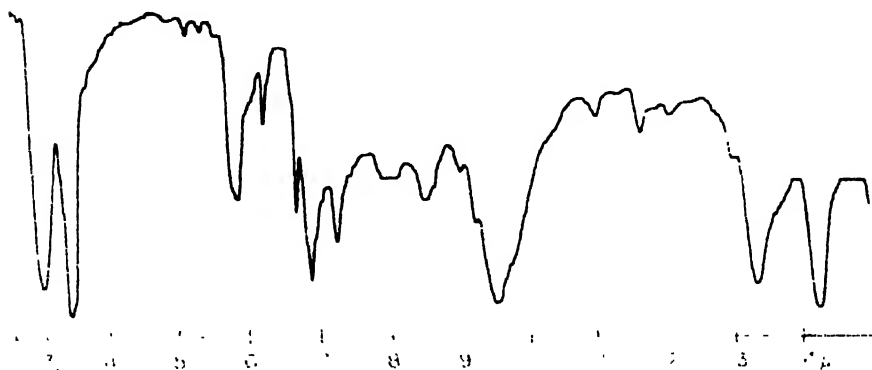


FIGURE 9-5. Rose absolute.

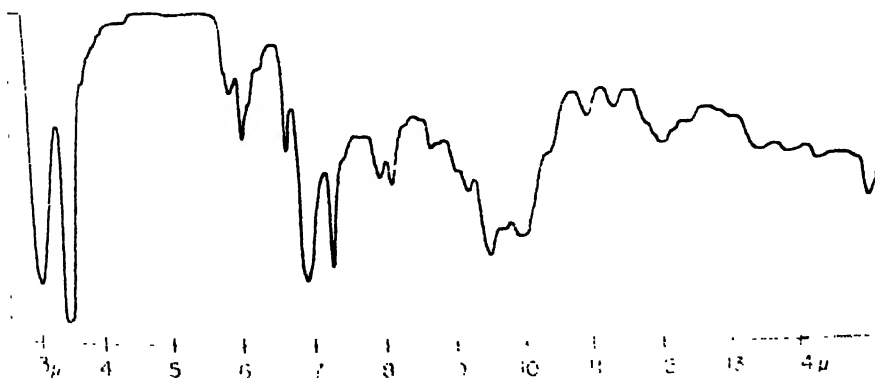


FIGURE 9-6. Distilled rose oil (Ro. Otto).

14.3μ (monosubstituted aromatic). Both oils absorb at 9.6μ (primary alcohol), the extracted oil because of its phenyl ethanol, the distilled oil because of its citronellol. Evaluation of extracted oils should be made by observing the ratio of phenyl ethanol to other components such as the carbonyl compounds (5.8 to 5.9μ). The distilled oil should be checked for

citronellol (9.6μ), geraniol (10.0μ), and phenyl ethanol content (13.4 and 14.3μ).

Lime oil is still another oil subject to variation with production method, available as a distilled (Figure 9-7) or expressed (Figure 9-8) oil. The distilled oil is produced by distillation of a pulp-juice mixture. Since the oil is distilled in contact with the acidic juice, and the distillation may require several

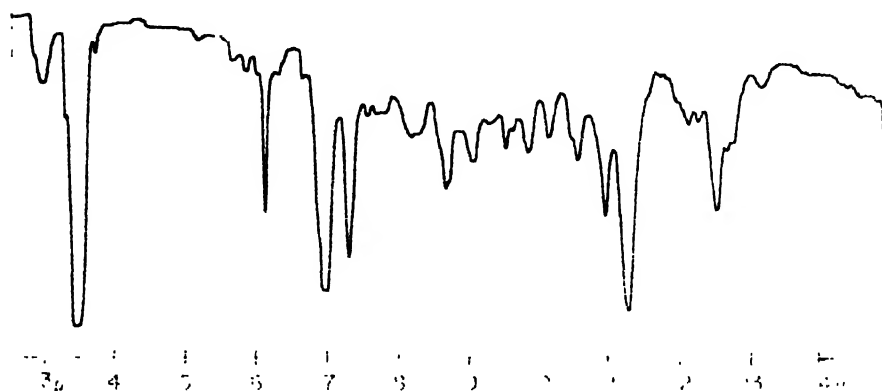


FIGURE 9-7. Oil of Limes distilled.

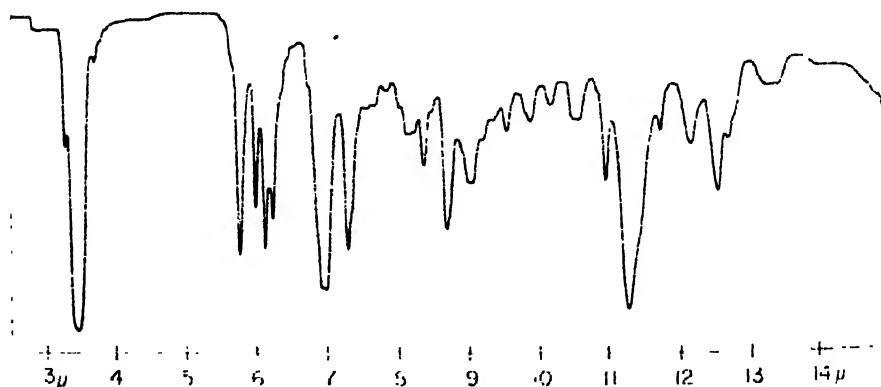


FIGURE 9-8. Oil of Limes expressed.

hours for completion, several chemical and physical changes occur. The high boiling substances, like the coumarin homologs, do not completely distill. These substances with bands at 12.15μ are much stronger in the expressed oil. The distilled oil shows a higher alcohol (2.9μ) content. These differences between the distilled and expressed oils are easily seen by infrared examination, due in this case to processing differences.

Effect of Plant Species. Differences are also possible when the processing is the same and the result is oil of different composition because of botanical differences.

Citronella oil is distilled from members of the same plant family with different species. The Java citronella oil (Figure 9-9) contains about 30 to 40% geraniol and 30 to 50% citronellal. The Ceylon oil (Figure 9-10) contains 30 to 35% geraniol and 5 to 15% citronellal. The infrared spectra

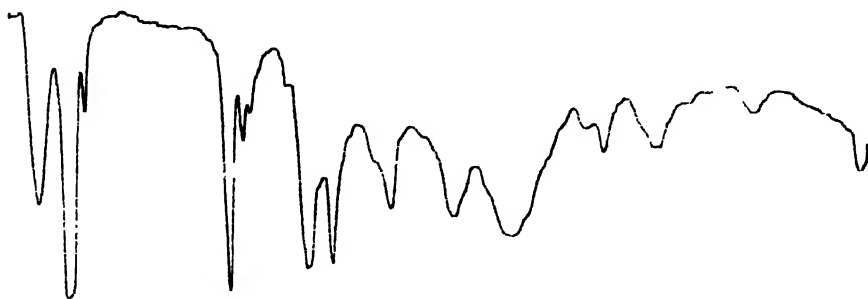


FIGURE 9-9. Oil of citronella Java.

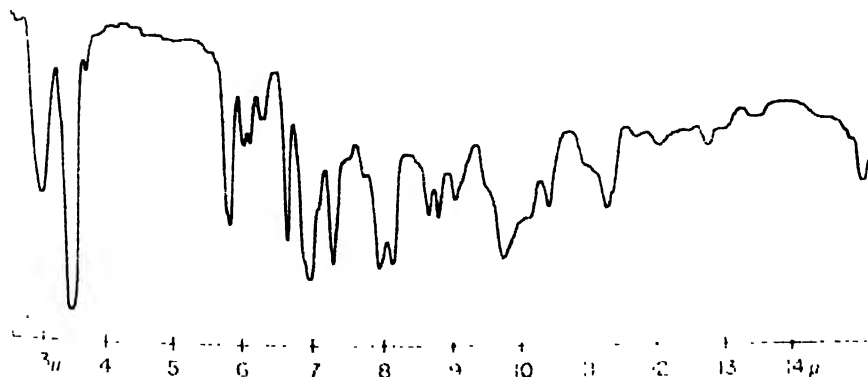


FIGURE 9-10. Oil of citronella Ceylon.

show these differences clearly. The Java oil with its high geraniol content shows strong bands at 2.9, and 10.0 μ , and a stronger band at 5.8 μ due to the higher citronellal content.

Effect of Plant Part. Differences in composition can be even more striking when essential oils are produced from different parts of the same plant. In the case of cinnamon oil (Figures 9-11 and 9-12), the bark oil is composed mainly of cinnamic aldehyde, while the leaf oil is mainly eugenol. The infrared spectrum of the leaf oil shows the eugenol content to be at least

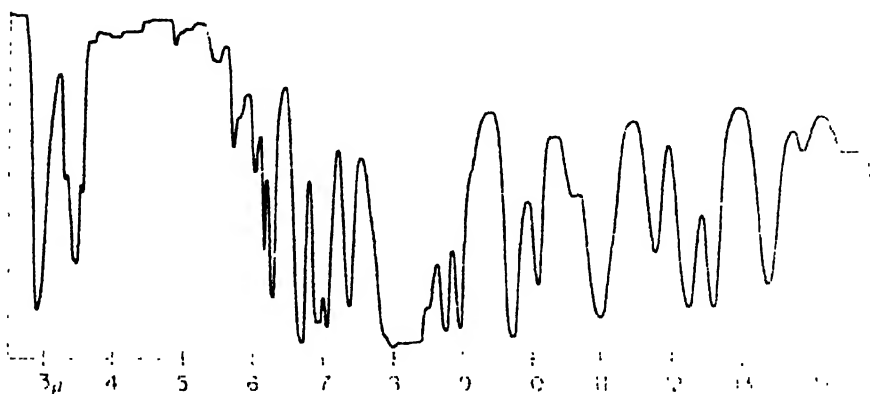


FIGURE 9-11. Oil of cinnamon leaf.

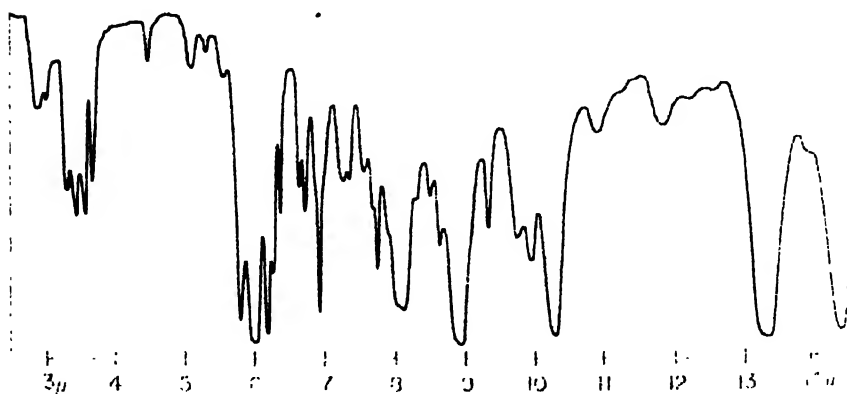


FIGURE 9-12. Oil of cinnamon bark.

80%, with very little else observable except perhaps a small amount of carbonyl. The cinnamon bark oil shows infrared bands due to eugenol at 2.9, 10.9, 12.2, and 12.6 μ . The eugenol content, however, cannot exceed 10% based on the strength of these bands. Some unconjugated carbonyl is present (5.8 μ), but the bulk of the curve is due to cinnamic aldehyde.

The bitter orange tree yields three different essential oils. The fruit yields an expressed oil very similar to sweet orange oil, being composed mainly of limonene, showing infrared bands at 6.1, 10.9, 11.3, and 12.5 μ and containing only several per cent of oxygenated components.

The bitter orange leaf is distilled to produce an oil known as oil of petitgrain bigarade (Figure 9-13), which is quite different from the oil of the fruit (Figure 9-14). The infrared spectrum shows only weak bands between 11.2 and 11.4 μ , indicating that the terpene content is perhaps only 1%

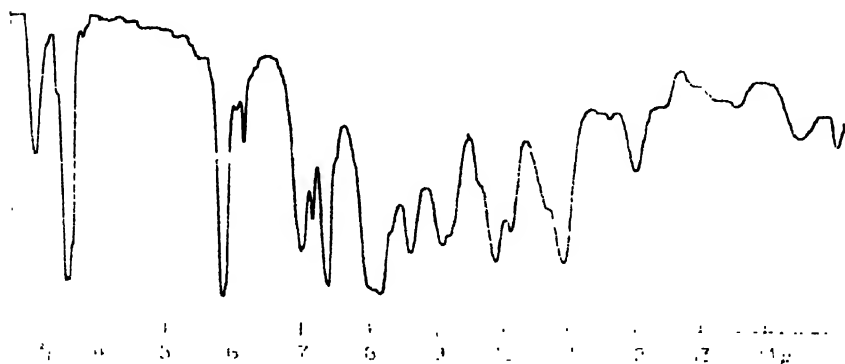


FIGURE 9-13. Oil of petitgrain bigarade.

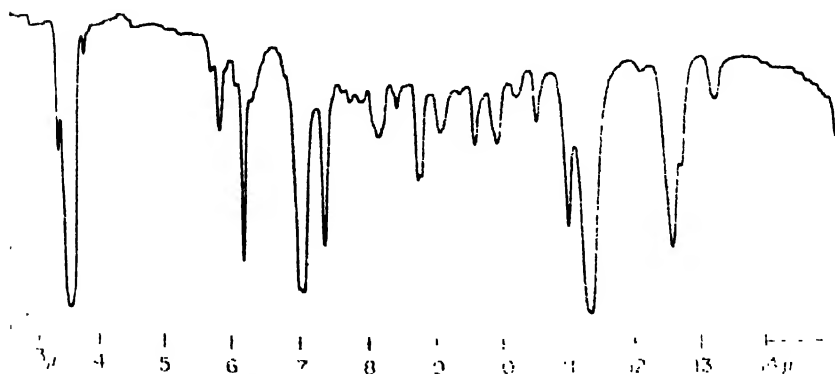


FIGURE 9-14. Oil of orange bigarade.

of the terpene content of the fruit. The bands at 5.8, 8.1, 8.6, and 9.8 μ indicate that linalyl acetate is the major component with linalool and other alcohols also present.

The flowers of this tree are distilled to produce an essential oil known as oil of neroli bigarade. The difference between this oil and the petitgrain bigarade are more subtle than the differences between either oil and the fruit oil. The difference in cost, however, is not subtle, and the purchaser of an expensive oil like neroli will be concerned with the possibility that the oil has seen more of the hand of man than is necessary for the picking and processing.

Detection of Dilution and Adulteration. The detection of essential-oil dilution is a very important phase of the infrared investigation. An essential oil is of value as a raw material for certain isolates, for its odor or flavor, or in some cases it may be used as a solvent. These properties may be barely affected or even accentuated by some forms of dilution. Dilution is practiced for the purpose of extending the quantity of essential oil on hand, or to affect the properties (chemical or physical) of quality favorably. Dilution may be practiced at one or more stages of the essential-oil's journey from botanical to user. It may be diluted by including foreign botanicals or substances at the harvest site to the distilled oil, to the broker's lot, or to the essential-oil house's stock.

The detection of such forms of dilution may be accomplished by careful infrared analysis. The spectra are examined for trace amounts of foreign substances, and the ratios of the absorption bands are determined to see if they fit the expected range of variation.

The dilution may be made with a substance which is a normal component of the essential oil, or with another oil rich in this component. For example, citral may be added to lemon oil for the purpose of representing the mixture to be a lemon concentrate. Here it is important to note the ratio of citral (5.98μ) to other carbonyls (5.8μ). A series of mixtures of lemon oil with different amounts of citral added can be put in the reference file for the purpose of authenticating lemon concentrates. If the proportions of carbonyl (5.8μ), alcohols (2.9 to 3.0), limonene (11.3), beta-pinene (11.75), and gamma-terpinene (12.8) are the same in the concentrate as in a lemon oil, yet the concentrate contains more citral, then the concentrate should be suspect.

Another case of dilution is that of the addition of cinnamon leaf to cassia. Since cinnamon leaf oil is mainly eugenol, showing bands at 2.9, 6.6, 10.9, 12.2 and 12.6μ , the relative strength of these bands in proportion to cinnamic aldehyde bands at 5.99, 10.3, 13.4, and 14.5μ , and the cinnamyl acetate bands at 5.8, 9.8μ , and the *ortho*-methoxy cinnamaldehyde band at 9.55μ which are present in the cassia oil, will be indicative of the degree of dilution of this type.

Lavender oil is often diluted with either lavandin or spike lavender. Larger quantities of lavandin can be added because the lavandin oil is

closer in composition and odor to the lavender than the spike oil is. The major components of both lavender and lavandin are linalyl acetate and linalool. The bands at 8.1 and 9.8μ are acetate bands and are due to the linalyl acetate. In oil of lavender (Figure 9-15), the band at 9.8μ is stronger than the band at 10.1μ (a vinyl double bond absorption), but

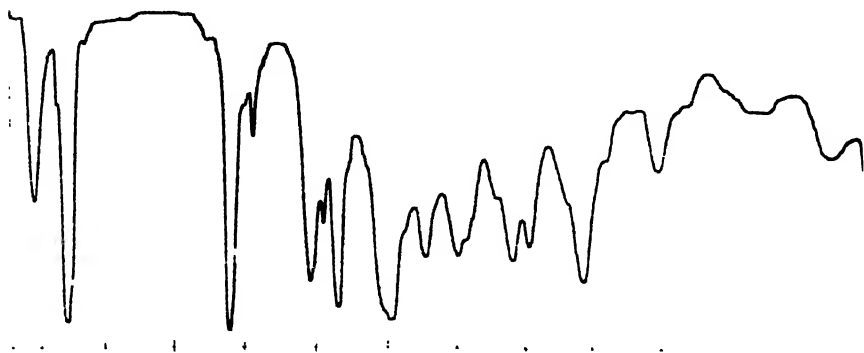


FIGURE 9-15. Oil of lavender.

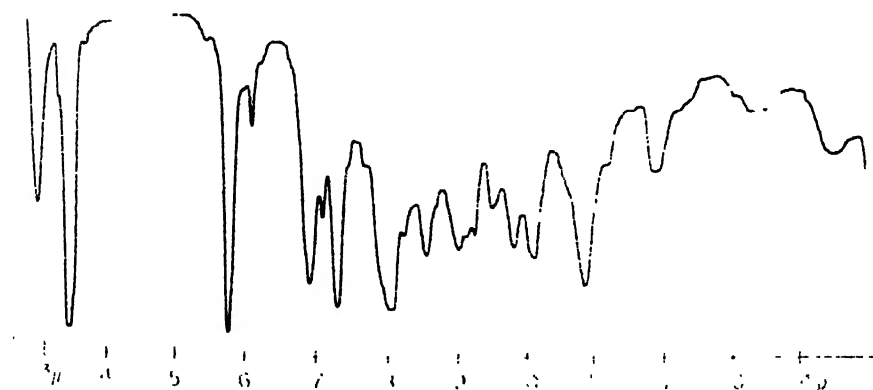


FIGURE 9-16. Oil of lavandin

lavandin oil (Figure 9-16) has this ratio reversed. Lavandin also has a small sharp band at 9.25 to 9.3μ due to cineole, and a band at 9.5μ due to camphor and borneol. Both of these bands are extremely weak in lavender oil, and the proportions of these bands must be carefully observed to detect dilution. Spike lavender dilution will show bands at 9.25 to 9.3 and 11.9μ , and the acetate band at 8.1μ will be diminished (Figure 9-17).

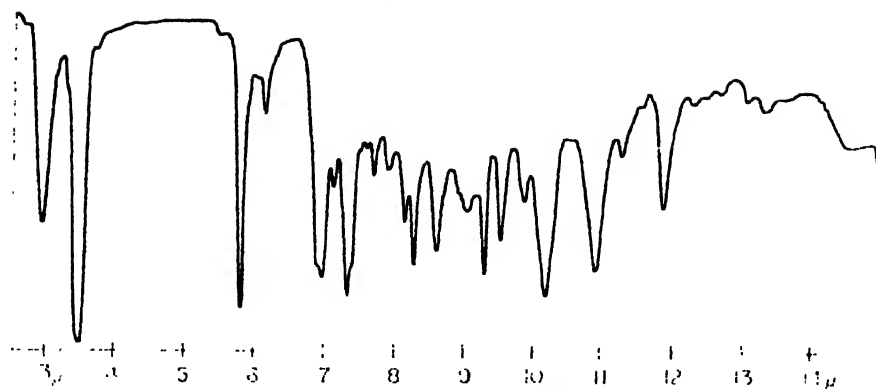


FIGURE 9-17. Oil of spike lavender.

Cananga oil (Figure 9-18) may be added to ylang ylang oil (Figure 9-19), since the odors of the two are compatible. Cananga contains a low concentration of oxygenated substances, while ylang ylang contains quite a bit. This dilution may be discovered by an increase in the terpene-sesquiterpene

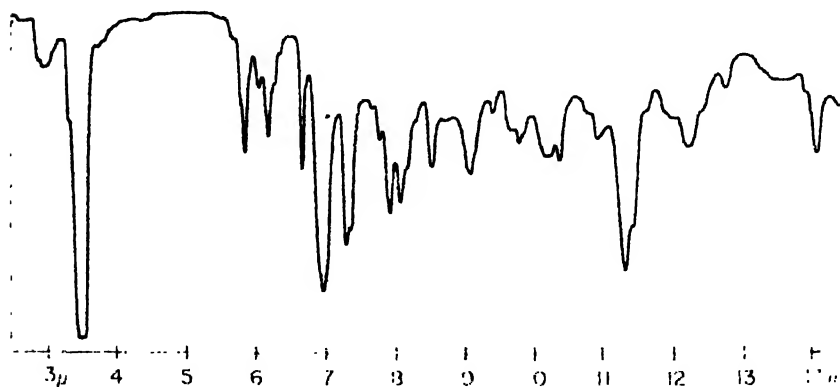


FIGURE 9-18. Oil of cananga.

band at 11.3 to 11.4 μ , a decrease in the carbonyl band at 5.8 μ , and a decrease in the acetate band at 8.1 μ . The monosubstituted aromatic bands at 13.4 and 14.4 μ will also decrease, as will the benzoate band at 14.1 μ .

The dilutions mentioned, while practiced, are not the preferred ones. These dilutions involve the addition of natural materials which fluctuate in price and availability and pose the threat of becoming too expensive at some unforeseen date because of a poor crop. The preferred dilution is the one using a synthetic material. The diluent would be available in quantity

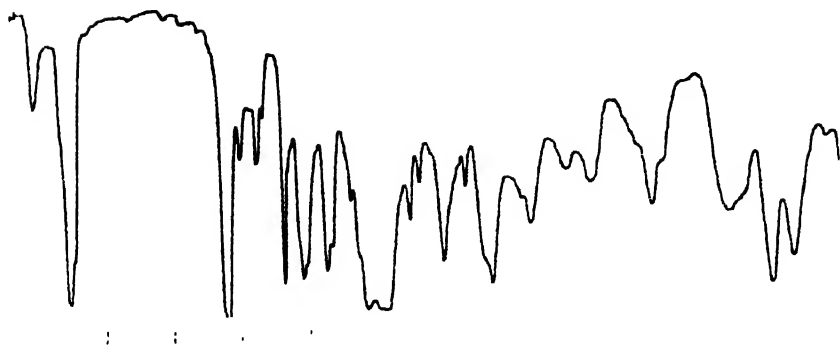


FIGURE 9-19. Oil of ylang ylang extra.

at a fairly consistent price, and very pure. Quite often the diluent is a natural constituent of the essential oil and the dilution will go unnoticed if practiced with restraint. Here the industry does not describe the dilution by the term "adulteration." Sophistication is the dilution with a substance which is a normal component of the oil. In this category of dilution can be mentioned the addition of phenyl ethanol to rose absolute. Rose absolute contains a large quantity of phenyl ethanol. A little more, added carefully, and the properties are hardly affected. Here the diluent is pure, cheap and available. As mentioned before, this dilution may be discovered by careful examination of the ratio of phenyl ethanol to other components.

Another common dilution is the addition of terpinyl acetate to lavender or bergamot oil. This addition causes a peak to appear at 3.9μ . A small amount will cause a small shoulder at 8.9μ instead of a peak. In this case only a few per cent will show up. Superposition of the suspected curve on a good curve will show this band even when extremely small.

While the careful addition of diluents may be virtually undetectable, infrared instrumentation has shown its value for the detection of such materials. It is at times a simple matter to detect adulteration as when an odorless diluent, such as benzyl benzoate, is added to an oil which contains few aromatics. A benzoate band at 14.1μ in lavender oil, for example, will indicate adulteration without question, and very rapidly. While infrared analysis is not the complete answer, it has considerably reduced the problem of detection of dilution.

Component Identification. The infrared identification of essential-oil components is of great interest to the users and manufacturers of essential oils. If the components of major importance are identified, it may be possible to create less expensive synthetic oils with the desired odor or flavor character-

istics, or it may lead to the fortification of these desirable characteristics by the addition of the important components to the essential oil. It may also be useful for determining the geographic origin or means of production of the essential oil. A good deal of this type of identification has been done by the essential-oil industry and has led to the production of many fine synthetic essential oils.

The first step in such identifications is the isolation of the pure component. This may be accomplished by chemical and/or physical means such as partition chromatography, gas chromatography, differential solubility separations, derivatization, and other methods. Essential oils can usually be easily separated into terpene and oxygenated components by chromatography on packed alumina columns. Petroleum ether will elute the terpene and sesquiterpenes, while the oxygenated components remain adsorbed. The oxygenated components can be eluted with the more polar solvents. This is generally the best approach, since there is more interest in the oxygenated substances than the hydrocarbons, because of their high flavor and odor value. Further separation can be accomplished by gas chromatography. The collected fractions can be checked for purity by reinjection. Even without beam condensing or microscope adapters the infrared curve may be obtained on samples well under 1 microliter in size by using microcells. This approach puts essential oil research within the budget of even the smaller businesses.

Once the infrared curve of the pure component is obtained, the identification of the substance becomes the next step. It is necessary to study the curve and make assignments for the bands to try to determine the structure of the substance. While infrared correlation charts are helpful, the best aid is a library of curves of known materials. Such a library may be effectively utilized for identifications of unknowns by arranging the library according to structure. In this manner, the unknown will be classified (for example, aromatic, monosubstituted, primary alcohol) and will be identified by comparing its spectrum to the spectra of the knowns in the file with similar structure. It is quite often necessary to search the literature for infrared curves. While it is best to make identifications by comparing known and unknown on the same instrument under quantitative conditions, it is not always possible and a literature search may be necessary.

Punch cards can be used to identify unknown substances. This is done by sorting (manually or by machine) through cards of known substances for the absorption bands which are present in the unknown. Each card is punched with holes to mark the absorption bands of the compound. The cards which are rejected during the sorting are the cards of compounds which have no bands such as the bands shown on the curve of the unknown. Slight shifts of wavelength on either the known or unknown may cause this

system to fail. If the bands are punched from carefully calibrated curves of pure knowns, and the unknown is likewise calibrated and characterized, the system is quite effective.

Aromatic Products. Another job for infrared is the evaluation of aromatic products. It is possible for the manufacturer and the purchaser to exercise quality control over many aromatic products. Complicated separations and identifications are usually unnecessary, since these products are pure materials, and even a single band can expose the presence of an impurity from the manufacturing process. It is relatively easy, for example, to check for the presence of aldehydes in alcohols, benzaldehyde in cinnamic aldehyde, or acetophenone in methyl phenyl carbinol, to name a few. The isomer ratios of some materials can easily be determined, such as terpinyl acetate in linalyl acetate, or isosafrole in safrole, or beta-terpineol in alpha-terpineol. The infrared curve may give information about any reactions that may have taken place to alter the product, such as dehydration or hydrolysis.

Flavor Mixtures. The analysis of flavor mixtures presents the spectroscopist with problems not encountered in the other analyses mentioned. The flavor mixture may contain materials which interfere with the analysis, such as citric acid, sugar, alcohol, and water which may obscure most of the bands of interest, and in the case of water, cause damage to the cells. The flavor principles may be present in very low concentration, and the flavor may be extremely complex because of the presence of many multi-component essential oils and extracts. Such a flavor may be rich in broad-banded polymers, gums, sugars and acids. There are also special forms of flavors such as the spray-dried products, too rich in gums for effective infrared on the product as is. Infrared analysis can be employed if the product is treated in some way to produce a more workable sample. One method of treatment involves water distillation of the flavor followed by extraction of the distillate with a solvent like isopentane. Removal of the solvent leaves an oil which is free from nonvolatile substances and ethanol. The aqueous portion of the distillate and residue may be separated by ion exchange or other methods, followed by infrared examination of the fractions.

Cosmetics. Cosmetics provide their share of special problems, since very few of these materials can be used as is for infrared analysis. Even if the insoluble fluoride or silver chloride cells are used, or reflectance methods are employed, the high water and alcohol content will obscure most of the spectrum. In addition to water and alcohol, the spectroscopist is up against infrared obscurers like inorganics, polymers, glycerols, and emulsifiers. Extraction and/or distillation methods can be used to concentrate the part of the cosmetic of interest. Perfumes and colognes can be concentrated fairly simply by adding a large quantity of water and extracting with petro-

leum ether. This may cause a small loss of water soluble components, but the extract is far easier to work with than the original sample.

A GENERAL PROCEDURE FOR QUALITATIVE INFRARED INVESTIGATIONS

A general method for the qualitative investigation of products can be developed involving a number of steps.

Sample Treatment, History, and Data

The sample should be treated to remove water, alcohol and interfering substances. Obtain all the available data such as chemical and physical constants. If it is an essential oil, check the literature for identified components, and the curve library for the range of infrared variation to be expected. If it is a synthetic material, determine its source and method of manufacture for the starting materials, solvents, and reaction products which may be expected as impurities.

Scanning the Sample

Check the instrument daily for wavelength accuracy and optimum performance, and run the sample under the best conditions to give sharp, strong peaks with the lowest possible background. Peak discernment is very important, and in general, most aromatics are best run twice on the same curve using two different path lengths. With a path length of .025 to .030 mm, impurities may be visible, but the stronger bands absorb completely and the exact position of the band is hard to determine because of its broadness. A path length of .010 to .015 mm will usually be small enough to give sharp peaks with even the stronger bands. If the sample is a solid, it is best run as a solution, preferably using carbon tetrachloride up to about 7 to 8 μ and carbon disulfide for the rest of the infrared region.

Interpretation Aids

The laboratory should have available as many aids to interpretation as possible, such as the Colthup chart¹, or books like "The Infra-red Spectra of Complex Molecules" by Bellamy² and "Chemical Applications of Spectroscopy - Techniques of Organic Chemistry" Weissberger.⁶

Examining the Spectrum

Examine the spectrum for strong or significant peaks starting at 2.5 μ . A broad band from 2.7 to 3.0 μ (sometimes higher) indicates N - H or O - H stretch and may be alcohol, phenol, acid amide or amine. Examine the region from 8 to 10 μ for confirming peaks for alcohol or phenol, 6.0 to 6.5 μ for confirming peaks for amine or amide, and 5.8 to 6.0 μ for acid.

A sharp band slightly above 3.3μ indicates olefins or aromatics. Examine the region from 4.9 to 6.0μ for phenyl ring substitution or vinyl or vinylidene overtones. Examine the region from 6.0 to 6.7μ for sharp peaks indicative of olefins, aromatics or conjugation. Olefins do not have bands from 6.6 to 6.8μ and usually are below 6.15μ .

When the band assignments appear to have delineated a complete structure, a comparison of the unknown spectrum with that of the suspected compound or its homologs may be made. As more experience is gained, fewer bands are necessary for the interpretation.

Mixtures

When a mixture of components is being evaluated, it is best to label the peaks of the knowns before working on the unassigned bands. Compare the intensities of the bands of the knowns with those of the unknown. It is possible that a band is relatively stronger than expected because of absorption from another substance absorbing at the same wavelength.

The sensitivity of a particular identification will depend upon the intensities of the bands of the unknown and the amount of interference from other components. Certain aromatic bands can be detected in a mixture containing a low concentration of aromatics in the range of a few tenths of a per cent, such as the parasubstitution bands of para-cymene at 6.6 and 12.3μ in lemon oil. Identification of a molecule in a solution of similar molecules may be insensitive below the level of 5 to 8%. Strong background absorption with broad peaks indicates high molecular weight compounds or very complex mixtures. Strong, broad peaks at 2.9 and 6.1μ , weak at 4.7μ indicate water. The background will be strong in the 3 to 15μ region.

TYPES OF INFRARED LABORATORY ORGANIZATION

The organization of a laboratory is dependent on factors which vary considerably from one business to another. The size of the company will generally affect such factors as the analytical budget, the number of people available to staff such a laboratory, and the number of departments which will be served by the laboratory. Management attitude and the traditions of the company also affect the picture, since a small progressive company may be more willing to invest in instrumentation than a larger company without this forward attitude.

The Specialized Infrared Laboratory

The laboratory may be organized as a special unit performing specialized analyses of a specific nature for the needs of the organization. Such a laboratory may be responsible for infrared analysis and nothing more.

enlisting the aid of other laboratories for the special treatment of samples such as gas chromatographic separation of fractions. This specialized laboratory more efficiently utilizes its equipment, deriving more complete information of a single type. Equipment is better maintained and technique is better, providing very useful information for theoretical and pure research purposes.

The Centralized Instrument Laboratory

Another type is the centralized instrument laboratory. This laboratory houses all of the company's instruments and is responsible for all instrumental analyses required by any of the departments. This laboratory will use several forms of instrumentation, if necessary, to perform the required analysis. This type of laboratory makes the best use of the complementary aspects of various instruments, and is thereby able to handle complete problems by using the most effective instrument for each phase of the problem. Here, there is the desirable tendency to make a separation or determination by the best instrumental method rather than laboriously stretching an analysis, using exotic techniques, to fit the only instrument—as is done by the specialized laboratory. The instrumental laboratory is, however, more apt to be overburdened because it handles such varied problems. Because of this it may be slow to produce routine analyses, being too involved in long term, complex problems.

The Decentralized Installation

A third plan is the decentralized installation, where instruments are assigned to a particular department for any analyses it requires. The big advantage is the speed with which samples are analyzed. The scheduling of analyses and the assignment of sample priority is no problem as it is with the other laboratories, since all samples originate from one group or department. Since there may be many departments requiring identical instrumentation, it is often too costly to employ any but the lower priced instruments. Because of this, the information derived may be less complete and the quality of the analyses may suffer.

Work Organization

Organization of the work will depend on the type of laboratory and the work load. The specialized laboratory and the decentralized laboratory can schedule samples in order of their submission, while the centralized laboratory may give priority to the quick analysis when all other projects on hand are long term. Each type of installation must yield to the pressure of samples that cannot wait, the centralized laboratory and the specialized laboratory feeling the pressure from several departments.

The filing of reports, curves, data and samples should be handled by as simple a system as possible while remaining efficient. Ideally, the filing of curves and reports should be done in triplicate, cross-indexed, with copies going into alphabetical, chronological, and structural files. While this may be the only efficient manner of filing data on research projects, the filing of data on a specific analysis on a production item may best be done chronologically. Each laboratory should strive for the most comfortable system that works for its particular needs.

THE FUTURE OF INFRARED

In the light of the newer forms of instrumentation available, infrared analysis should be reevaluated:

(1) While it never will be the complete answer to all analytical problems, it is still the best single shot analytical method for mixtures like essential oils.

(2) Its lack of sensitivity to some substances can be greatly improved by proper sampling and instrumental techniques.

(3) New sampling techniques allow analysis of a broad range of materials.

(4) While NMR and Mass Spectrometry have their specialized values, they are expensive and possess greater sampling difficulties.

(5) In conjunction with Gas Chromatography, infrared extends the capabilities of both instruments, making a potent research team.

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CHAPTER

10

Infrared in Coal Structure Research

*R. A. Friedel**

INTRODUCTION

Infrared spectroscopy has played an important part in the investigation of coal structure since the first extensive investigations by Cannon and Sutherland^{17,18} in 1945. The quantitative and qualitative infrared analysis of coal chemicals was in use even before that; an article on the analysis of phenols by Thompson *et al.*¹¹ appeared in the same issue with an original article on coal spectra.¹⁷ The early infrared investigations of coal^{17,18,19} used nearly all of the techniques that are still used today, namely, the thin section, the mineral oil mull, and destructive distillation. The most notable additions in recent years have been the halide pellet technique, and the use of many different extracts; also, attenuated total reflectance (ATR) and infrared luminescence have been applied to coal.

The next work on the infrared spectra of coal was done at the Pittsburgh spectrometry laboratory of the Bureau of Mines. The spectra of coal and extracts were given along with structure assignments,⁷⁹ followed later by other work on coal and carbohydrate chars.^{34,97} Work was also being published on techniques and band assignments by Hadzi,⁶¹ Gordon *et al.*,^{59,60} Cannon,¹⁹ Bergmann *et al.*,⁶ van Vucht *et al.*,¹⁰⁸ J. K. Brown,¹¹ Friedel and Queiser,¹⁵ Roy,⁹¹ Brooks, *et al.*,¹⁰ Fujii,⁵⁴ Kinney and Doucette,⁶⁵ and others. Bergmann *et al.* were the first to use the KBr pellet technique. Van Vucht¹⁰⁸ and Gordon^{59,60} published the first collec-

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tions of spectra of many different ranks (carbon contents). Recent advances in coal structure research by infrared have been in the assignment of absorption bands in the coal spectrum,^{40,64,101} based on extensive spectra-structure correlations and on the knowledge gained from infrared spectra of coal before and after various chemical reactions.

Coals of the same rank from various parts of the world have similar properties and infrared spectra. A sample of high volatile bituminous vitrain from Illawara, Australia, will have the same spectrum as a similar vitrain from West Virginia. Coal is a difficult substance to study spectroscopically. It is desirable to study the material in a solid state rather than in solution or in the molten state. Coal is a very insoluble substance and complete solution in any particular solvent is never obtained. Investigations on extracts of coal are always in question, because the extract does not represent the entire coal; however, pyridine is a fairly good solvent and will dissolve a significant fraction of many coals. Coal decomposes on heating so that vapor state studies are impossible. If coal is heated to the molten state, complicating reactions occur and immediately produce something that is no longer coal.

Coals are nonhomogeneous organic materials. They consist of various petrographic constituents (macerals) which can be differentiated under the microscope: (1) *vitrinite*, the principal coal maceral, is a bright, vitreous substance derived from woody tissue; (2) *exinite* is the fossil remains of spores and cuticles; (3) *fusinite*, found in fossil charcoal, is carbonified cell walls; (4) *micrinite* is a dull constituent derived from strongly decayed plant material. These are the principal macerals. Vitrinite, a macroscopic constituent of coal obtainable in large pieces for coal research work, consists almost entirely of vitrinite with minor amounts of the other macerals. The spectra of the organic constituents of coals differ principally in having differing intensities for various bands.^{3,25,78}

The classification or ranking of coals for research purposes is usually based on the elemental analyses, particularly the carbon content. The names of the various coal ranks in the United States are derived from their volatility characteristics at high temperatures. The ranks and the approximate ranges of carbon, hydrogen and oxygen contents are given in Table 10-1. These are the three most important elements in coals. Nitrogen, sulfur, and minerals are also common constituents; they are generally present in small amounts but the concentrations vary widely.

This chapter will be devoted essentially to a discussion of studies of coal structure by infrared spectroscopy and the information on coal structure to be obtained from investigation of coals, coal derivatives, and similar carbonaceous materials. Special techniques required will be discussed in detail. The analysis of coal chemicals will not be discussed to any appreciable

TABLE 10-1. RANKS OF COALS AND THEIR GENERAL RANGES OF ELEMENTAL ANALYSIS

	Carbon	Hydrogen (Moisture and Ash-free Basis) (wt. %)	Oxygen
Lignite (brown coals)	< 77	> 5	> 19
Sub-bituminous	78-80	5-6	11-18
Bituminous	80-91	4-6	3-10
High volatile (A, B, or C)			
Medium volatile			
Low volatile			
Anthracite	> 91	2-4	2-3
Semi-anthracite			
Anthracite			
Meta-anthracite			

degree because the problems are quite similar to those involved in the analysis of petrochemicals.

EXPERIMENTAL TECHNIQUES

For the investigations of solid coals three techniques have been used principally: (1) Ground thin sections, (2) mulls, and (3) halide pellets.

Ground Thin Sections

This technique has been used with success in the Bureau of Mines laboratories. Although not used extensively, it has been instrumental in serving as a standard for coal spectra. Spectra obtained with thin sections do not have the interfering bands of a mulling agent or a halide pelleting compound. One of the greatest advantages of the thin section method has been its avoidance of the scattering problem in the short-wavelength infrared region where the use of either mulls or pellets is difficult. Formerly, the general background absorption that increases toward short wavelengths in mull and pellet spectra of coals was attributed to scattering of particles, or to scattering plus unknown electronic absorption. In 1956 the thin-section technique was used to demonstrate that Pittsburgh coal vitrain (84% carbon) does not scatter above 2μ , and that strong electronic absorption occurs below 2μ .^{15,37}

The preparation of a ground thin section involves the grinding of the section by hand, using a glass plate with some adhesive to hold the coal. Grinding is done down to a thickness of about 15 to 20μ for bituminous coals, and then the adhesive is dissolved in a solvent and the section floated away from the glass plate. H. J. O'Donnell has prepared sections for Bureau spectral work by pipetting the solvent out of an evaporating dish and guiding

the coal section or fragment down onto a slotted brass disc.^{34,99} Salt plates can also be used. The coal section is taped to the mount and is then ready for the spectrometer. Disadvantages of the method include: (a) It is not applicable to all coals; (b) the thickness may not be uniform and thickness determinations by various methods are limited to accuracies of a few per cent for very thin sections;¹⁸ (c) the fragmentation of the prepared thin section sometimes leaves no crack-free portion large enough for examination by conventional spectrometry; in such cases microspectrometry is applicable; (d) difficulties may arise in obtaining a section with low mineral content. Despite these difficulties reproducible spectra can be obtained, and the method serves as a good standard for coal spectra.

Oil and Halocarbon Mulls

Cannon and Sutherland^{17,18} used the mull technique, although the results were not very good because of tremendous scattering due to large particle sizes. J. K. Brown¹¹ succeeded in obtaining very good spectra by this technique and presented an excellent collection of many coal spectra over a large range of ranks. As usual with mull work, there is considerable difficulty with interference of the mineral oil bands. It is common, however, to utilize perfluoro or perchloro mulling agents to obtain spectra in those regions where hydrocarbon oils interfere. One great advantage of the mull technique is that finely ground particles are protected from exposure to air and water, and the heat of grinding is dissipated in the mulling agent.

Coal is an extremely difficult substance to grind. In order to obtain good spectra it is necessary to hand grind with mortar and pestle as long as eight hours.¹¹ This requirement moves coal into a separate class relative to most chemicals which require only a few minutes or seconds of grinding with a mulling agent. The pelleting technique also requires that coal be ground for long periods.

Halide Pellets

The pellet technique has become the most popular method of obtaining infrared spectra of coals.^{2,6,7,8,10,30,35,36,59,60,65,68,108} Potassium bromide has been used principally. KBr and coal are ground together, then pressed into a pellet in an evacuable die. At the Bureau of Mines pellets customarily are made 0.5 mm thick with coal concentrations of 1%. Disadvantages in the use of pellets of coal are: (a) Coal requires many hours of grinding with attendant increase of contaminants; (b) spurious bands not attributable to contaminants are produced in the mixing and grinding of halide and coal. Fortunately coal is an amorphous substance and does not undergo any spectral changes due to crystalline modifications, which are common difficulties in pelleting.

Long Grinding and Contamination. The grinding of KBr and bituminous coal of 84% carbon must be carried on for at least 16 hrs in order to eliminate scattering in the 2 to 6 μ region. Under these conditions contamination from the container is not noticeable. However, grinding for longer times can produce contamination and resulting background absorption and scatter. Local high temperatures are undoubtedly produced by dry grinding and can easily cause some decomposition or oxidation.

Spurious Bands. Although KBr does not possess any band in the 2 to 15 μ spectrum, the mixing and grinding together of KBr and water-containing substances such as inorganic hydrates and coal produce very intense false bands at 2.95, 4.90, and 6.12 μ .⁷³ The false bands are easily detected by comparing the spectra of pellets and mulls; for example, the mull spectrum of Na₃PO₄·12H₂O has its H₂O band at 3.13 μ , but in a pellet the H₂O appears at 2.95 μ , resulting in erroneous assignments. The three false bands are undoubtedly due to H₂O and will be referred to as KBr-H₂O bands. The intensity of these bands increases almost directly with time of grinding. Even with KBr alone a pellet with a negligible H₂O band at 3.0 μ will, upon grinding for one minute, show a six-fold increase in H₂O band and this band will be centered at 2.95 rather than at 3.0 μ .

KBr is not nearly as hygroscopic as generally supposed; 100 g of KBr in saturated air take up only 0.007 g of water.⁹² The main trouble experienced with KBr pellets does not need to involve water in the KBr itself. KBr has been allowed to sit on a laboratory table for days without picking up sufficient moisture to cause any appreciable increase in H₂O absorption in the spectrum of the pellet; however, grinding the KBr produces intense H₂O absorption in the resulting pellets. Milky has shown that the interfering bands are much less intense if coarse KBr is used.⁷⁷ Careful and extensive drying of the KBr and of coal samples, as well as preparation of the mixture by grinding in inert atmospheres does not seem to prevent the development of these bands with extended grinding.

The effect of pressure in pellet preparation was investigated by comparing spectra of a KBr pellet of coal and of the KBr-coal mixture in a mull. No difference was observed. KCl-coal pellets were also made; the same false bands occurred, with the most intense band shifted to 2.97 μ .

It has been found, in our laboratories, that the production of the KBr-H₂O bands is attributable to interaction involving KBr and the water in the sample. Water is present in coal as such even if the coal is dried under vacuum at 105°C. Roberts⁸⁹ has reported the occurrence of the same bands in pellets of steroids and has attributed them to traces of water in the sample. Durie has reported the same bands in the preparation of KBr pellets of polynuclear aromatics.²⁷

Figure 10-1 indicates the effect of extremely long grinding and the accompanying great intensity of the $\text{KBr-H}_2\text{O}$ bands at 2.95, 4.90, and 6.12 μ . The intensity of the 2.95 band is very great. The spectrum in Figure 10-1 was obtained with an 0.5 mm pellet of one part coal and 200 parts KBr. Of this one part coal, approximately 2% is moisture, or a total of only 0.04% water in the pellet; the resulting specific extinction coefficient, K , is about 4.0 liters/g cm. The sharpness of the 2.95 μ band that develops with very slight grinding may indicate that it is due to oriented water molecules on the surface of the freshly cleaved KBr crystallites. Thus the $\text{KBr-H}_2\text{O}$ bands are presumably produced by trace amounts of water molecules, from the sample or in the KBr, which become oriented.

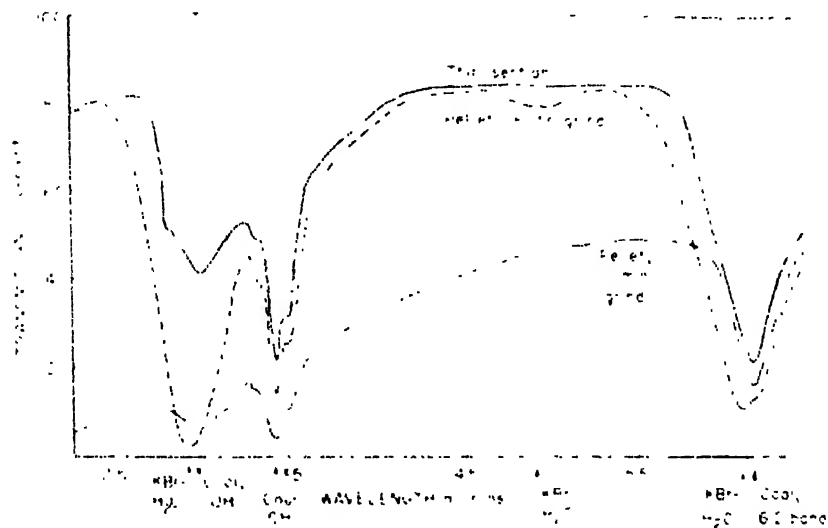


FIGURE 10-1 Effects of the $\text{KBr-H}_2\text{O}$ complex on the spectrum of Pittsburgh coal vitrinite.

An x-ray investigation was made of these mixtures; no lines that might be assigned to a new crystal structure were found.

Heat Treatment Effects. Because of the suspected orientation of the water molecules a logical attempt was made to eliminate them by heat treatment of the pellets. Such treatment successfully decreased the intensity of the bands but did not eliminate them. Roberts, however, found in the case of steroid pellets that these bands could be eliminated completely by heating to 100°C.⁸⁹ Although this treatment was not completely successful in the case of coal pellets, the bands are eliminated completely by determination

of the spectra in hot cells operated at 175°C.¹⁰² Although the bands are eliminated at these temperatures, it is found that with cooling of the sample the bands again reappear, although at reduced intensity.

Preparation Under Solvents. The elimination of the water bands from spectra by means of hot cells is satisfactory though rather inconvenient. Attempts have been made to prepare pellets which would not possess these bands. Grinding of the coal and KBr separately, followed by mixing without grinding, is not successful. Grinding the two components together is necessary for the diminution of scattering at short wavelengths. The freeze-drying technique is not very applicable to coals since they are mainly insoluble in any solvent.

One promising method appears to be that developed by Durie.²⁷ KBr pellets of the sample prepared in the usual way were found to have absorption at the water band positions. If, however, grinding of the sample with KBr was done under a covering liquid, carbon tetrachloride, water bands in the resulting pellet did not appear, perhaps indicating that the troublesome water was coming from the atmosphere. Experience with adding H₂O to KBr had indicated that water *per se* was not troublesome. As shown by the preparation of a pellet using Durie's technique with a liquid containing 5% water (95% ethanol) the resulting KBr pellet of coal had no false KBr-H₂O absorption. Thus the mere presence of water is not responsible for these bands. It is suggested, therefore, that the success of Durie's technique may be due to the fact that the covering liquid provides a means of conducting the heat, of grinding away from the KBr surfaces and prevents activated adsorption of the H₂O molecules on the KBr surfaces. It is equally possible, however, that the adsorption process requires H₂O in the vapor state.

The difficulty with this method for pellets when applied to coal is that a substance such as carbon tetrachloride apparently cannot be eliminated from the coal completely at temperatures below thermal decomposition of the coal. Thus one is faced with the prospect of replacing one set of bands with another. Other liquids such as hydrocarbons may be better. Use of water itself as a covering liquid has some promise, although initial attempts were frustrated by the necessity of grinding the sample after the evaporation of the water because of the recrystallization of the KBr. If this process is tried in a freeze-drying system it may be successful.

Low Temperature Preparation. Grinding at liquid nitrogen temperatures has also been attempted in the hope that properties of the coal would be altered sufficiently so that grinding would occur more readily. This unfortunately was not found to be the case. In routine preparation of coal samples for spectral measurements the KBr-H₂O bands are most easily avoided

and time is saved by grinding for short times, in spite of the scattering at short wavelengths (Figure 10-1, bottom spectrum).

STRUCTURE ASSIGNMENTS

Spectral information on the structure of coal is obtained by reference to spectra-structure correlations. Band assignments were originally made strictly on this basis, but eventually organic and physical-chemical methods were called upon to assist the infrared interpretations. Methods that will be discussed in conjunction with infrared determinations on coal include solvent extraction, petrographic separations, pyrolysis, vacuum distillation, chemical and electrolytic reduction, catalytic hydrogenation and dehydrogenation, oxidation, chlorination, charring of model compounds, photolysis, nuclear irradiation, flash and laser irradiation, electrical discharges, charge-transfer complexing, and microbiology.

Qualitative Information

Structure assignments are included in Figure 10-2 and Table 10-2; these are principally the assignments reported previously,^{11,19,35,62,79,108} along with assignments based on more recent studies of chemical reactions. There remains some disagreement, and the preferred assignments in Table 10-2 are not necessarily exclusive. Alternative assignments are given.

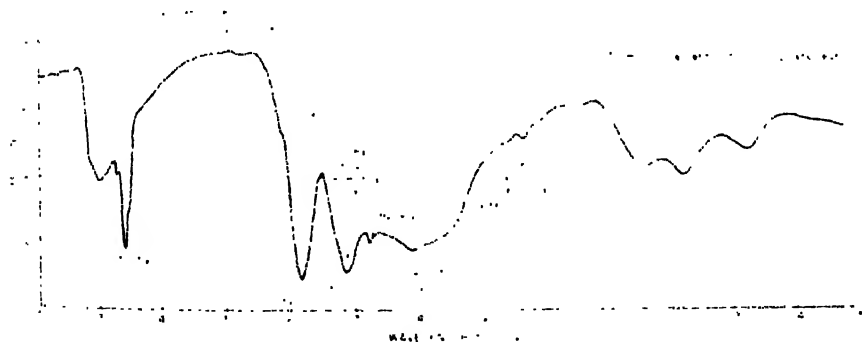


FIGURE 10-2. Infrared spectrum of anthraxylon from Pittsburgh seam coal, assignments of bands to molecular structures.

One of the greatest uses of the infrared spectrum has been the indication of the absence of certain groups which were thought to be present. At various times such groups as simple alcohols, ketones, esters, acids, paraffin

TABLE 10-2. SPECTRAL ASSIGNMENTS FOR THE INFRARED SPECTRA OF COALS

Wavenumbers (cm ⁻¹)	Wavelength (μ)	Assignment
> 5000	2.0	Electronic absorption; overtones of vibration bands (weak)
3300	3.0	Hydrogen-bonded -- OH (or -- NH); phenols
3030	3.30	Unsaturated CH, probably aromatic
2950 sh.	3.38 sh.	CH ₃
2920	3.42	
2860	3.50	Naphthenic and/or aliphatic CH ₂
2780 to 2350	3.6 to 4.25	More strongly hydrogen-bonded -- OH than that at 3.0μ
1900	5.25	Aromatic bands, prevalent for 1, 2-di- and 1, 2, 3-trisubstitution
1780	5.6	
1700	5.9	C=O
1610	6.2	C=O ... HO- (and or aromatic CC' with --O-- substituent), (Carboxylates)
1590 to 1470	6.3 to 6.8	Shoulder at 6.65, but no bands except in lignites; most aromatics have bands here
1450	6.9	CH ₂ and CH ₃ ; also aromatic CC or ionic carbonate
1375	7.27	CH ₃ groups
1330 to 1110	7.5 to 9.0	CO in phenoxy structures (for low rank coals) () in aliphatic structures)
1040 to 910	9.6 to 11.0	Clay minerals such as kaolinite; some phenoxy structures
860	11.6	Aromatic CCH in single and/or condensed ring-structures: Possible substitution on phenol and hydrocarbon structures: 1,2,4-, 1,2,4,5- (1,2,3,4,5-); i.e., isolated aromatic H's
833 (weak)	12.0 (weak)	(1,4-, in high rank coals)
815	12.3	1,2,4-, (1,2,3,4-); i.e., isolated H and/or 2 neighbor H's
750	13.3	1,2-
700 (weak)	14.3 (weak)	(Mono- or 1,3-disubstituted aromatics, minerals)
690 to 400	14.5 to 25	General absorption; mineral bands
400 to 80	25 to 125	(See text under <i>Other Infrared Methods</i>)

chains, and olefins have been considered in coal structure work; but infrared spectroscopy has shown such groups to be present in small amounts, if at all. Such structures might still be present as parts of more complex structures.

The collection of spectra of many different ranks of coal (Figure 10-3)⁵¹ is also helpful because of the possibility of correlating gradual spectral changes with changes in functional group bands and elemental analyses. Some of the definite changes observed for increasing rank are the increase of the aromatic relative to the aliphatic CH, the decrease in hydroxyl

absorption, the surprisingly slight changes in the long-wavelength aromatic bands and in the 6.2μ band.

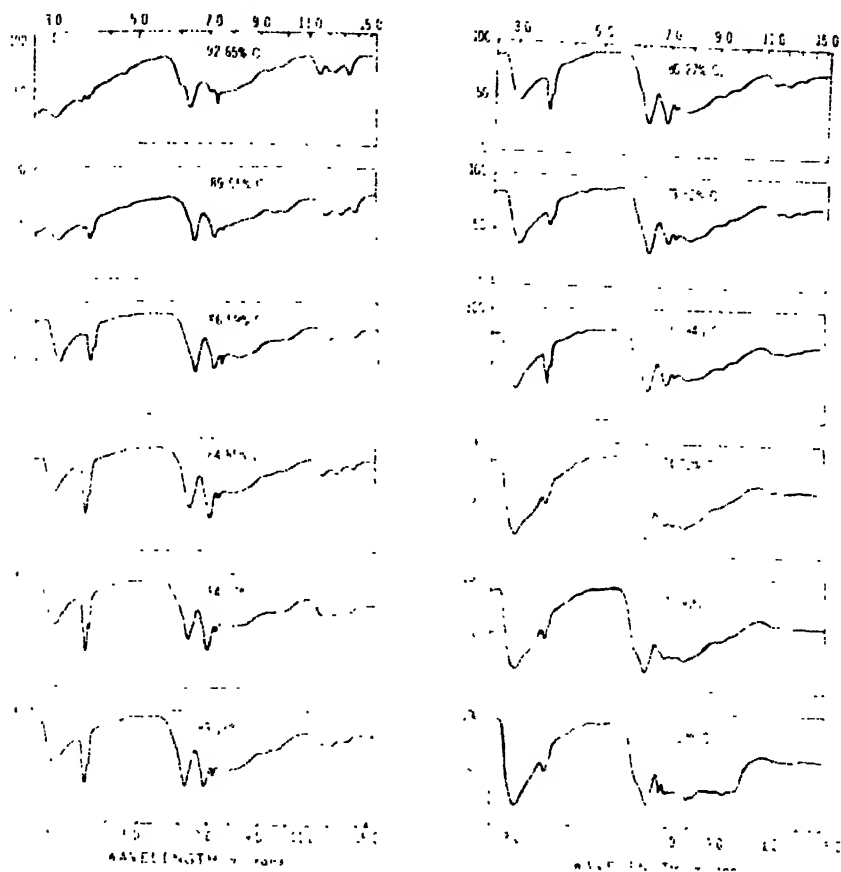


FIGURE 10-3. Infrared spectra of coals of various ranks (carbon content).⁵⁴

Discussion of some of the individual bands follows:

Below 2.0μ , Electronic Absorption and Overtones of Vibration Bands. The presence of electronic absorption has been demonstrated in the spectra of chars⁶⁷ and of coals.^{28,35,37} In Figure 10-4, transmittance of a thin section of bituminous coal drops sharply below 2μ . No combination of overtone bands could entirely account for the observed absorption, and scatter is minimized as a possibility by the use of a thin section. This result is presumably consistent with the semiconductor properties of coals. The energy difference between the filled and empty electronic shells is shown by this

spectrum to be sufficiently small so that the energy gap lies in the edge of the infrared region. The energy gap for Pittsburgh vitrain is located at about 0.85μ and thus has a value of 1.5 electron volts.³⁷ For an anthracite thin section the energy gap is 0.3 electron volt (4.5μ).³⁶

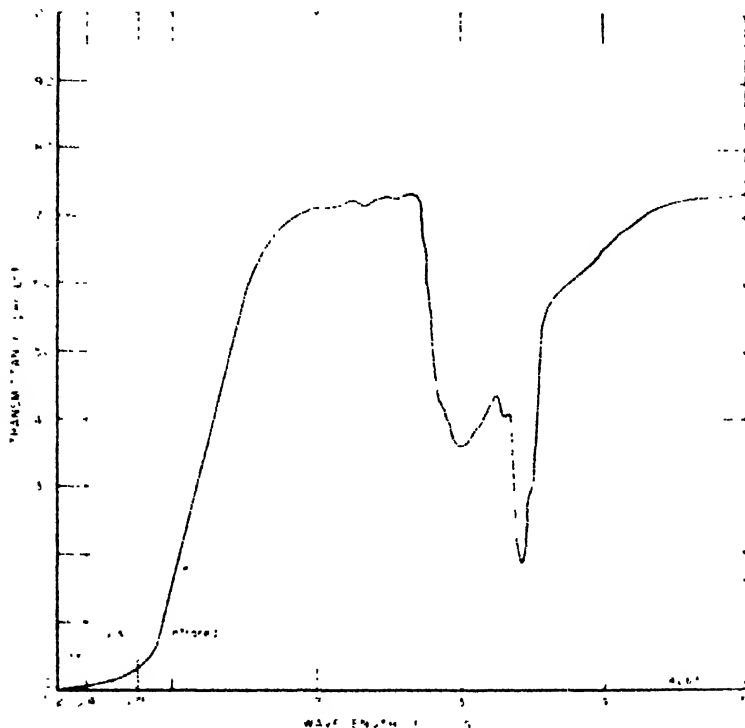


FIGURE 10-4. Electronic absorption and energy gap shown by thin section of Pittsburgh coal vitrain.³⁷

3μ , Hydroxyl Groups. From the apparent lack of aliphatic C—O absorption at 9.0 and 9.5μ and the presence of phenolic C—O absorption in the 8μ region, the OH group in coal is assigned to phenols. Combined infrared and chemical evidence has shown that the OH is indeed phenolic.¹² Much of this absorption may also be due to water that is not removable from the coal at ordinary temperatures. A point of difficulty in connection with this band in the spectra of KBr pellets of coal is the interference of the anomalous KBr-H₂O bands developed by grinding.

The broad absorption from 3.5 to about 4.25μ is apparently due to —OH (or —NH) groups that are more strongly hydrogen-bonded than the —OH

groups contributing to the 3.0μ band. Hydroxyl groups in strongly chelated structures might be responsible for this absorption.³⁵

The 3.25 to 3.5μ Region, CH Groups. (See "Structure Assignments, Quantitative Information.")

5.9μ , Carbonyl Groups. In the medium and high rank coals absorption at this wavelength is very weak, when present. Simple aliphatic carbonyl groups are seldom present in appreciable concentrations. This band often develops because of oxidation of the coal in handling. Preparation of thin sections does not cause this; grinding of KBr and coal can produce carbonyl absorption unless carried out in an inert atmosphere.

6.2μ Band. This assignment remains controversial. It is still not definitely determined whether the band is due to aromatic structures and/or a chelated and conjugated carbonyl structure. (Discussed more fully under "Quantitative Information.")

6.9μ Band. The usual assignment of this band solely to CH_2 and CH_3 groups is incorrect; additional structures are involved. (Discussed under "Quantitative Information.")

7.5 to 9.0μ Region. This region is assigned to aromatic ethers and phenols.

9 to 11μ Region. Some of the broad absorption from 9 to 10μ is probably due to C—O groups. But the bands at 9.67 and 10.0μ are the principal bands in the spectra of kaolins and other clay minerals.³⁵ Kaolinite also produces weaker bands at 10.7 and 11.0μ which are found in the spectra of coals with appreciable mineral contents. Other minerals, identifiable in various spectral regions, include carbonates and silicas.

11 to 14μ "Aromatic" Bands. These bands have always been assumed to be due to aromatic structures.^{11,19,35,79,108} It has been debated whether or not these aromatic structures were simple benzenoids or polynuclear condensed structures. This point is not likely to be settled by infrared spectra alone. It is not necessary to assume the presence of polynuclear aromatics in order to explain these bands; benzenoid structures can account for them. Types of substitution which are assignable to these groups of bands, whether in benzenoids or in polynuclear condensed aromatic structures, are given in Table 10-2. Assignments are based on spectra of both phenols and hydrocarbons.

The infrared spectrum cannot discern whether or not these bands are actually aromatic bands, although an aromatic origin is strongly suggested by the parallel increase with rank of the intensities of the 11 to 14μ bands and the 3.30μ aromatic CH band. An attempt was made to obtain further information on this question by means of spectra of chars prepared from a completely deuterated paraffin. (See "Chars of Model Compounds.")

15 to 25μ . In the spectra of raw bituminous coals from the Pittsburgh seam, weak specific absorption is found between 15 and 25μ , but it is

assignable to minerals,³⁹ because the bands decrease or disappear from the spectrum of the vitrain, which has a low mineral content. General absorption occurs throughout the 15 to 25 μ region.³⁵

Quantitative Information

Information on intensity is also of importance in studying the structure of coal. The spectral intensities, K values, for the absorption bands of Pittsburgh vitrain are given in Table 10-3.³⁶ Intensities of various absorption bands and the structural information obtained from them are discussed with regard to Pittsburgh vitrain and other coals:

TABLE 10-3. INTENSITIES OF INFRARED ABSORPTION BANDS
(K, IN LITERS/G CM) FOR
PITTSBURGH HVAB VITRAIN THIN SECTIONS³⁶

Wavelength (μ)	(K liters/g cm)	Base-line Anchor Points (μ)
3.0	0.14	2.7 --- 4.75
3.3	.038	3.2 - 3.6
3.42	.17	3.2 - 3.6
5.3	.004	5.05 - 5.5
6.2	.49	5.5 - 10.8
6.9	.36	5.5 - 10.8
7.27	.013	7.18 - 7.37
7.9	.26	5.7 - 10.8
9.67	.052	5.5 - 10.8
10.0	.030	5.5 - 10.8
11.6	.098	10.8 - 14.75
12.3	.092	10.8 - 14.75
13.3	.056	10.8 - 14.75
14.3	.008	10.8 - 14.75

The CH Stretching Bands. The combined intensities (peak absorbances) of the aliphatic and aromatic CH bands do not approach the amount expected for Pittsburgh vitrain, having 5.5% hydrogen.⁴⁰ By comparing the CH intensities of many types of model compounds and correcting the coal spectrum for the H in OH, the CH bands in the coal spectrum are found to represent only about half the expected intensities. The C-H absorption per H atom of a pyridine extract is about 25% higher than that for the original Pittsburgh vitrain, even though the hydrogen contents are essentially equal. Also, the CH bands in coal hydrogenation asphaltene do show the high intensity expected for the known hydrogen content of the substance, based on model compounds. In both these cases the CH bands have essentially the same half-width as the bands for Pittsburgh coal vitrain. The low peak intensities of the CH str bands in solid coal vitrain thus require that

(a) the missing hydrogens must be a type with which we are unfamiliar, or (b) hydrogen-containing groups are absorbing in regions not customarily expected for such groups, or (c) coals are sufficiently inhomogeneous so that measurement of the true absorption is not attained.

Recent comparisons of absorption area intensities for extracts of Pittsburgh vitrinite with pure compound data have shown that assignments can be made to specific structural types.^{82,103}

The 6.2 μ Band, Aromatic CC or Chelated Carbonyl.^{11,21,35,52,85} The intensity of absorption of the 6.2 μ band might be due to (1) a high concentration of aromatic structures and/or (2) a chelated conjugated carbonyl structure, such as in acetylacetone, kojic acid, or hydroxyacetophenones, etc. If such oxygenated structures are important contributors to this band then the aromaticity of coal does not need to be large. With assignment of this strongest band to an oxygenated structure the principal structures in coal might be aliphatic. Other structures which must be considered here are the phenolic or phenoxy structures which have intense 6.2 μ bands.^{11,35,51} The comparatively weak aromatic absorption from 11 to 14 μ assignment of this and the weak absorption at the 9.7 μ phenoxy region do not encourage the band to aromatic structures; however, this weak absorption may mean only that the aromatic rings are highly substituted.

The chelated carbonyl is probably the more logical assignment. The amount of oxygen required for chelated, conjugated carbonyl structures is very slight because the 6.2 μ band produced by these structures is extremely intense ($K \approx 25$ liters g cm, for oxygen in chelated C=O); whereas in Pittsburgh vitrain the "intense" 6.2 μ band is actually rather weak, $K = 0.49$ liters g cm (Table 10-3). Thus, only 2 weight per cent oxygen is needed to produce the 6.2 μ band in the spectrum of Pittsburgh vitrain. Similar small amounts of oxygen could produce the 6.2 μ bands for other coals, as well as for chars of oxygenated compounds. The conclusion that oxygen is not involved in the 6.2 μ band²² does not appear to be justified. Absorption areas require greater than 2% oxygen as the coal band is very broad and therefore more intense with respect to area absorption. Studies of chars of model compounds, to be described below, indicate that oxygen is involved in the absorption at 6.2 μ .

Additional structures to be considered include the carboxylates.¹⁰ Bonds between the organic and inorganic constituents of the coal may be involved in the 6.2 band; there is chemical evidence indicating that carboxylates may be involved.²⁹ Interference of the KBr-H₂O complex, described above, is unfortunately a frequent contributor to absorption near 6.2 μ .

Information from Relative Intensities. Relative intensities of the CH stretching and bending vibrations give important structural information. The base-line

intensities for the CH stretching vibration at 3.4μ customarily are stronger than those of the CH bending vibration in the 6.9μ region. In the spectra of coals the reverse is found (Table 10-3). This reversal is not known to occur in any reference compounds, as the str intensity is always greater than the bending intensity, as pointed out by Eloffson.³⁰ Thus there must be some other species absorbing strongly at 6.9μ in addition to the CH groups. What this grouping might be is not known. It could be a small amount of a mineral carbonate which absorbs very strongly in this region. Another possibility would be an aromatic structure.

The relative intensities of the bands in the 9 to 11μ region in the spectra of vitrain and of whole coal led to the assignment of mineral structures to these bands. Coal petrography, a purely physical method, was used to assign these bands. The only spectral differences occurred in the 9 to 11μ region and the intensities followed the mineral content of the samples. Reference spectra indicated that the minerals were principally of the kaolin type.³⁵ It is possible with a petrographic microscope to remove pieces of mineral from a powdered coal in order to study the effect of changing mineral concentrations on the coal spectrum.

The relative intensities of the aromatic bands are of use in assigning structures. In the lower rank coals the predominating band is that at 12.3μ , which is assignable to structures such as 1,2,4-trisubstituted aromatics. In higher rank coals a shift in intensities occurs and the 13.3μ band becomes very intense, indicating the predominance of disubstituted aromatic structures (benzenoid and/or polynuclear).

OTHER INFRARED METHODS

Two relatively new infrared methods have been applied to the study of coal: (1) Far infrared, (2) Infrared luminescence and (3) attenuated total reflectance.

Far Infrared to 125μ

Pittsburgh coal vitrain has been investigated out to 125μ .⁷⁶ Although there is general absorption throughout this region there is no indication of specific bands, nor the occurrence of energy gaps. In the 15 to 25μ region Pittsburgh coal does have weak absorption bands, as reported above, but these are apparently assignable to minerals rather than to organic structures in the coal.³⁹

Graphite was also investigated out to 125μ . No absorption bands nor energy gaps were found.

Infrared Luminescence

In the usual method of investigation for visible luminescence under mercury light it is easy to observe strong luminescence for solutions of

hydrogenation asphaltene and of coal extracts. It is difficult or impossible, however, to detect luminescence for solid coal, asphaltene, or extract. With the new method of infrared luminescence developed by Gibson⁵⁵ solid asphaltene has been found to luminesce as strongly as a solution of asphaltene. Solid extract and coal vitrain also luminesce, though very weakly.⁵⁶

The occurrence of luminescence in the infrared and not in the visible may be indicative of species that have strong electronic absorption at long wavelengths. Possible species are very large polynuclear condensed aromatics, very long conjugated systems, charge-transfer complexes, and/or free radicals. Free radicals are thought to be the most logical source of this luminescence.

Attenuated Total Reflectance (See "Sorbed Species")

COAL EXTRACTS AND DISTILLATES

A large amount of infrared work has been done on coal extracts.^{14,17,65,79,104} In general it can be said that the higher the percentage of coal the extract represents, the greater will be the similarity of the infrared spectrum to that of the original coal. For those extracts obtained from solvents which will extract only one or two per cent of the coal the similarity is not very great. One reason for the use of extracts is the avoidance of temperature effects in the preparation of spectral samples. Even though it is impossible to dissolve coals completely in any solvent, the avoidance of temperature effects can be important. One of the important solvents is pyridine which extracts about 25 to 30% of soluble material from bituminous coals. Such an extract is conceded to represent a sizeable proportion of the coal, and information obtained from it is therefore considered valid. Qualitatively, the spectra of the pyridine extract and of the original coal are practically identical.¹⁴ However, pyridine extracts of Pittsburgh vitrain show almost a 25% increase in intensity per H atom for the CH str band. Apparently pyridine preferentially extracts materials having more intensely absorbing CH structures.

Extracts can be examined as pellets, mulls, films or solutions. Pyridine is quite opaque in the infrared and there is little opportunity to observe the broad coal bands in the spectra of pyridine solutions among the sharp bands of pyridine. Mull spectra of extracts are usually good. Homogeneous, nonscattering films of pyridine extract are difficult to obtain by casting. However, fairly homogeneous films can be obtained by placing a warm solution of extract on two quartz plates to form a sandwich; then, upon slowly sliding the two plates apart, solid pyridine extract is deposited as a clear film. The principal use of spectra of extracts is to reinforce the information obtained from spectra of coal itself; but this information must be used cautiously as the extract does not represent the whole coal.

Distillates are also used for the study of the structure of coal. Because of the high temperatures involved there is danger of decomposition of the coal structure. Whether or not this is important in the case of infrared spectra is debatable, because it has been shown that there are only slight differences in the spectra of coal and of distillates prepared at about 500°C.^{13,81} The spectra are also similar to the spectra of coal derivatives obtained at similar temperatures, such as the spectrum of hydrogenation asphaltene⁸² and spectra of resins from low temperature tar which have been studied by Karr.⁶¹

REACTION PRODUCTS

More spectral information on the functional groups in coal can be obtained by the use of chemical reactions, with investigation of the infrared spectra before and after reaction.

Temperature Effects; Spectra of Residues

Temperatures over 300° to 400°C begin to produce decomposition in most coals. The spectra of the products of decomposition differ markedly from the spectra of the original coal. Effects of temperature on functional groups in coal have been studied by carrying coals through a temperature program.^{1,15,35-91} It is found, for example, that the band assignable to OH structures in bituminous coals disappears at about 500°C. The band attributable to phenoxy structures at 8 μ decreases in intensity at 300°C but does not disappear even at 550°C. The CH str band intensities decrease.^{12,33,34}

The longest-wavelength aromatic band, 13.3 μ , increases with temperature; it also increases with increasing coal rank. The 6.2 μ band demonstrates its great stability in remaining unchanged through temperatures approaching 600°C. The increasing background absorption hinders the study of coals at higher temperatures; the electronic absorption for a bituminous coal treated at 600°C renders the spectrum practically opaque to about 9 μ .¹⁵

Catalytic Hydrogenation; Reduction

Hydrogenation is an important reaction of coal that was used extensively in Germany during World War II to produce fuels and chemicals. The reaction is usually carried out at temperatures of 400° to 450°C at hydrogen pressures of several thousand pounds; the reaction is really a hydrogenolysis in which hydrogen stabilizes the reactive species that are produced. It is a useful reaction in conjunction with infrared spectra for studying coal structure. The infrared spectrum of asphaltene obtained from coal hydrogenation at 450°C resembles the spectrum of the original coal (Figure 10-5).³⁵ Asphaltene prepared at 400°C has almost the same spectrum as

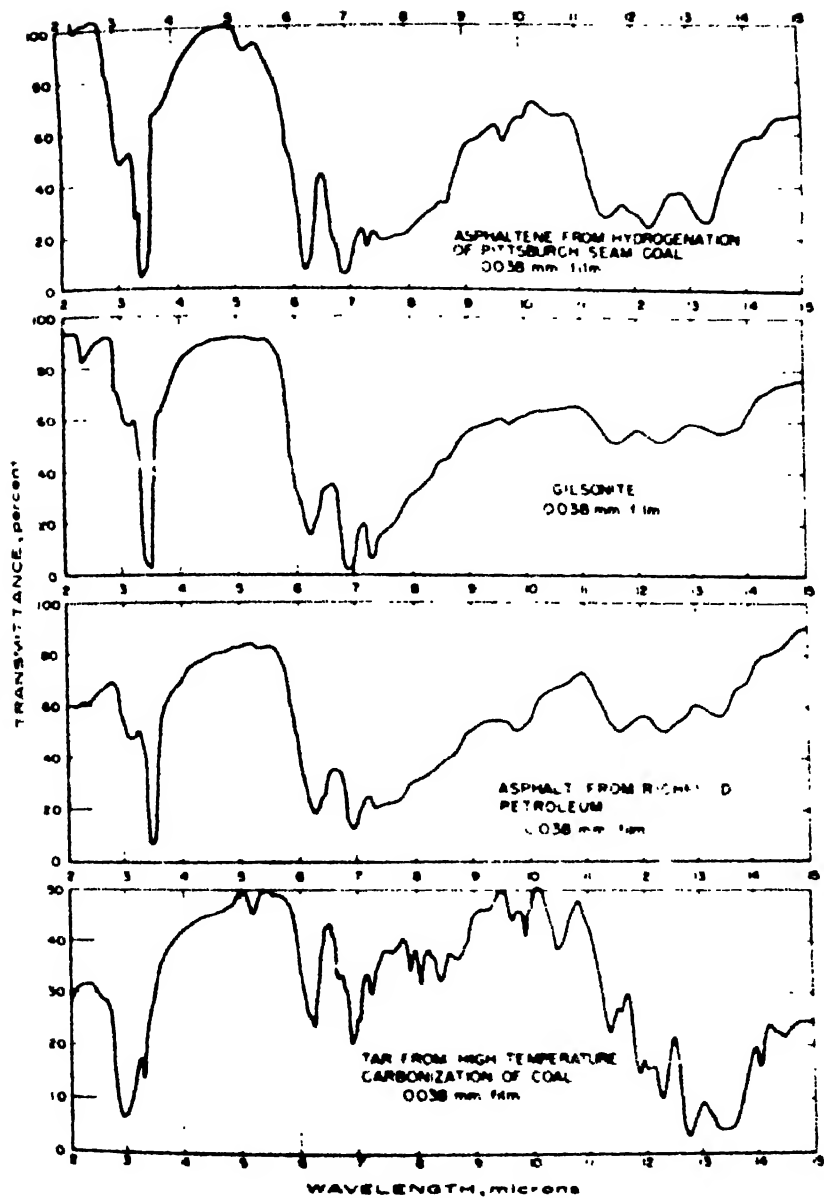


FIGURE 10-5. Comparison of infrared spectra of 450°C coal hydrogenation asphaltene with gilsonite, petroleum asphalt, and coal tar.¹⁵

vitrain except for increased aliphatic and aromatic CH str and bending bands at 3.3, 3.4, 6.9, 7.3 and in the 11 to 14 μ aromatic region. Other bands, including the 3.0 μ OH band, the 6.2 μ band, and the 8.08 μ phenoxy band appear to be relatively weaker, but actually these bands have practically the same intensities as they have in the coal spectrum. The 6.2 μ band becomes slightly sharper in the asphaltene spectrum while the aromatic bands increase, indicating perhaps that these bands do not arise from the same structure. However, as shown by the work of Reggel *et al.*,⁸⁷⁻⁸⁸ in the reduction of coal with lithium-ethylenediamine, the CH bands also increase and the 6.2 μ band decreases, but in this case the aromatic bands at long wavelength decrease along with the 6.2 band (Figure 10-6).

The definite similarity of spectra of coal hydrogenation asphaltene to the spectra of petroleum asphalts has been noted (Figure 10-5).¹⁴ The spectral differences are quantitative rather than qualitative; the petroleum asphalts have greater amounts of aliphatic structures and less of aromatic structures. Also given in Figure 10-5 is a spectrum of coal tar obtained from high temperature carbonization; the spectral fine structure is indicative of the chemical compounds produced from coal at high temperatures.

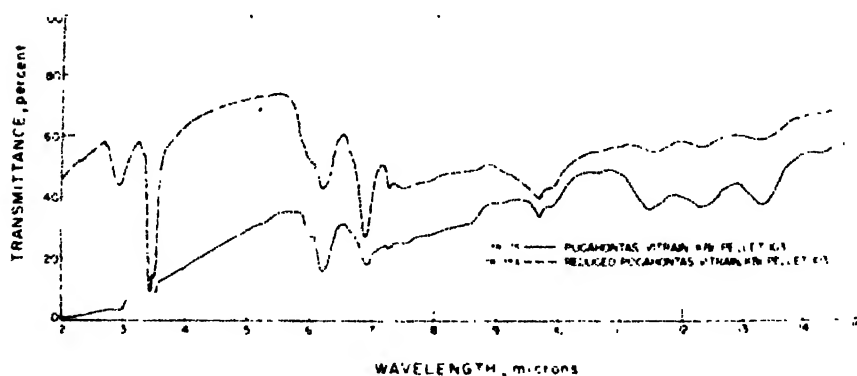


FIGURE 10-6. Infrared spectra of Pocahontas coal vitrain (90.5% carbon) and of a fraction obtained from reduction with lithium and ethylenediamine.⁸⁵

Hydrogenation of a carbohydrate has given interesting speculative information relative to coal structure. Nearly identical liquid (Figure 10-7) and solid products were obtained from the hydrogenation of sucrose and coal.⁸⁴

Chemical reduction of coal has been carried out by Reggel, *et al.*, using lithium-ethylenediamine^{87,88} and by Given, *et al.*, using lithium-ethylamine.⁸⁷ The infrared results indicated that in spite of extensive reduction the remaining aromatic character of the coal was pronounced.

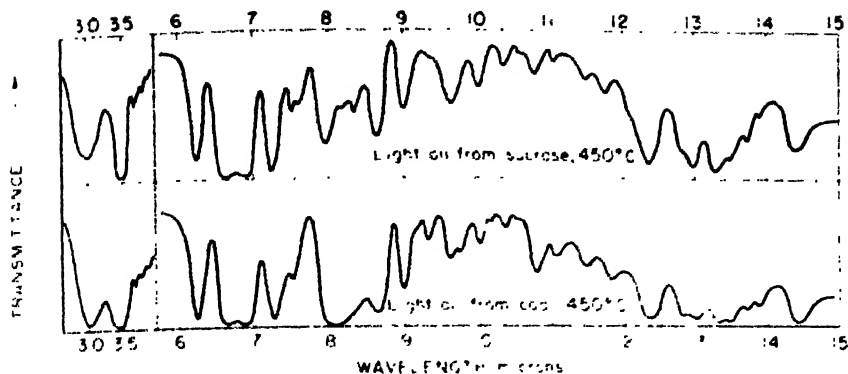


FIGURE 10-7. Infrared spectra of light oils from hydrogenation of coal and sucrose.⁸⁴

Extensive electrolytic reduction has been successfully carried out on coal.⁸⁵⁻⁸⁷ Infrared has been of considerable help in characterizing the reduced coal. The aliphatic character of the product promotes good transmission throughout the spectrum; the extent of reduction is clearly indicated. However, there has as yet been no identification by infrared of new compounds or specific structures in reduced coals.

Catalytic Dehydrogenation

Extensive catalytic dehydrogenation has been carried out on coal.⁸⁸ Infrared spectra of KBr pellets suffer from scatter and have not been particularly helpful in characterizing the products. The loss of hydrogen should mean that aromatic structures are being produced by dehydrogenation, but infrared has not been able to detect such structures. Artifacts are an added difficulty in this work for the solvents used thus far have entered into the catalytic reaction. The resulting chemical compounds, or polymers, then cling tenaciously to the coal. Though these substances are small in amount, their strong intensities stand out prominently in the nonspecific spectrum of the dehydrogenation product.

Oxidation

Oxidation of coal produces expected changes in spectra:^{1-20,53,91-108} increase in OH absorption, decrease of the aliphatic CH, an intense new band at 5.9μ for aliphatic carbonyls principally in carboxyl groups, and an increase in the broad absorption in the 8μ C=O absorption region. The long-wavelength aromatic bands appear to decrease significantly with oxidation, although the band at 6.2μ does not change.⁶⁻¹⁰⁸ Fujii has shown that the 6.2μ band increases with oxidation;⁶⁴ this may be a real change, or

it could be an apparent change caused by the intense band produced at 5.9μ by oxidation.

Hydroxyl Group Determinations

Acetylation of coals and infrared investigation^{10,12} of the products have provided important indications that OH groups in coals and coal extracts are almost exclusively phenolic. The spectra of acetylation products show by the presence of an absorption band at 5.68μ that the ester groups become bonded to aromatic rings.

An important reagent for determining hydroxyls is hexamethyl disilazane.^{71,94} The product from this reagent has incorporated in it silicon groups whose absorption bands are admirably suited for quantitative analysis.⁵¹

Chlorination and HCl Treatment

In reaction with PCl_5 , brown coals have been shown to possess active aliphatic hydrogens which can be replaced by chlorine.¹⁰ CH absorption bands decrease in intensity and C—Cl bands appear.

The reaction of brown coals with HCl shows a strong increase in the absorption intensity at 5.9μ .^{10,40} Alkali treatment removes the band completely and reacidification produces reappearance of the band, indicating carboxyl groups. A sharpening of the 6.2μ band with acidification indicates a probable contribution from carboxylates.

CHARS OF MODEL COMPOUNDS

Indirect studies on coal structure can be made through spectral investigations of chars of various kinds.^{11,29,34,35,39,40,42} Information pertinent to the origin of coals and other carbonaceous deposits can be obtained from such studies. It is commonly thought that a char from almost any material will give a coal-like infrared spectrum, but this is not the case. Chars prepared from various carbohydrates and other oxygen-containing compounds at 300 to 500°C invariably produce spectra having the strongest band near 6.2μ . Not all of these chars will show the other characteristic coal bands, particularly the aromatic bands at 11.6, 12.3, and 13.3. Carbohydrate chars all show these bands. Chars made from compounds that have ratios for OH/C of less than 0.3 usually do not show these aromatic bands. Apparently a sizable percentage of OH groups in the starting material is necessary to produce a good coal-like char.⁴² The close comparison of the spectra of coal and carbohydrate chars exists over a large range of temperatures; for example, the aromatic bands in the spectra of cellulose charred at 300°, 400°, and 500°C resemble respectively the aromatic bands in the spectra of coals of 70, 85, and 92% carbon (Figure 10-8).

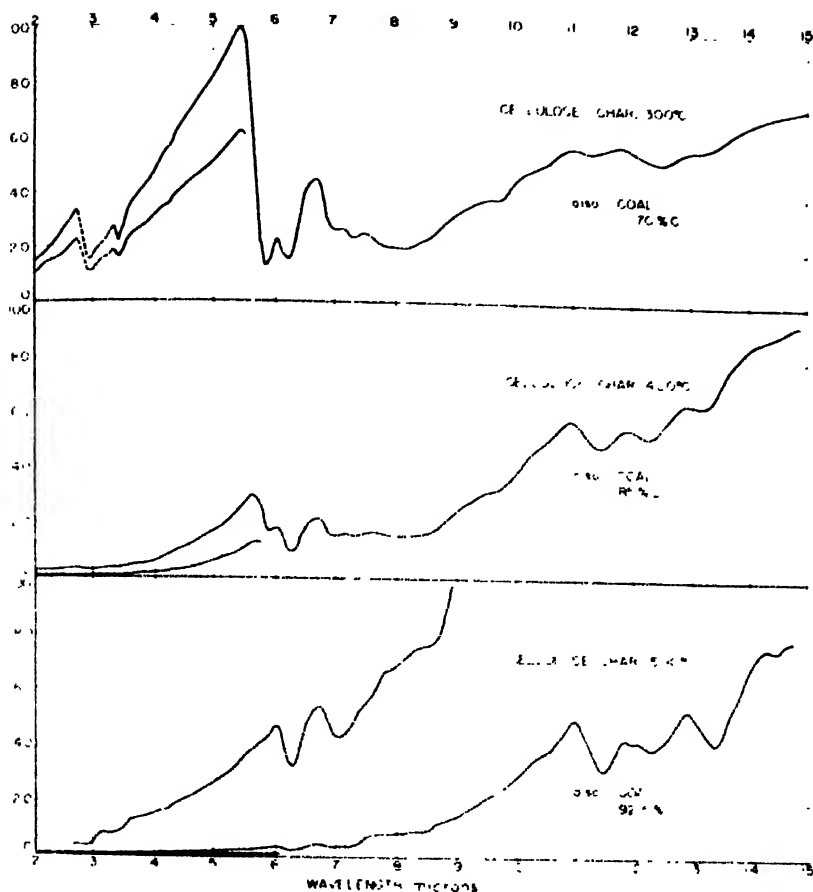


FIGURE 10-8. Infrared spectra of chars at various temperatures; correlation with coals. Per cent transmittance values refer to the partial spectra, 2 to 6μ ; other spectra are expanded arbitrarily.⁴²

Chars prepared from an aromatic hydrocarbon, anthracene, at 500°C in the absence of oxygen, yield a spectrum with no coal-like bands (Figure 10-9). On the other hand, char prepared from an aliphatic hydrocarbon, *n*-octacosane, at 450°C does produce most of the typical coal-like spectrum (Figure 10-10). However, the spectrum is not completely coal-like as the 6.2μ band is much weaker than the other typical coal bands (6.9 , 7.3 , 11.6 , 12.3 , 13.3). This finding indicates that a major part of the 6.2μ coal band might be due to an oxygenated (carbonyl) structure; the weak 6.2μ band that does occur in the octacosane char may be due to aromatic structures.

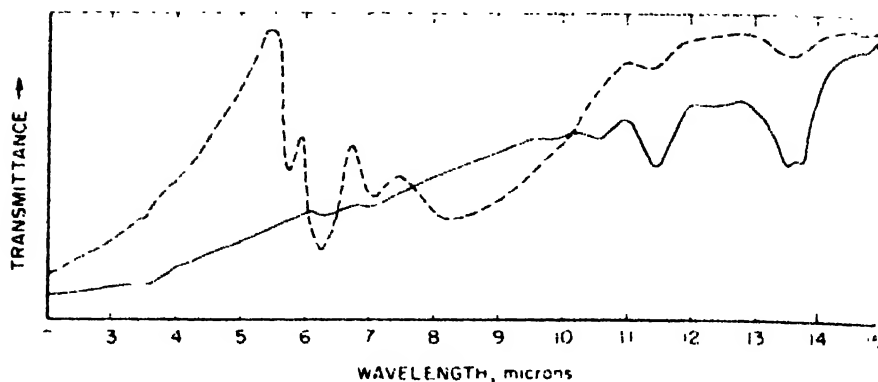


FIGURE 10-9. — Anthracene char, 500 C in inert atmosphere;
 --- Anthracene char, 500 C in air after preheat at
 300 C in air.

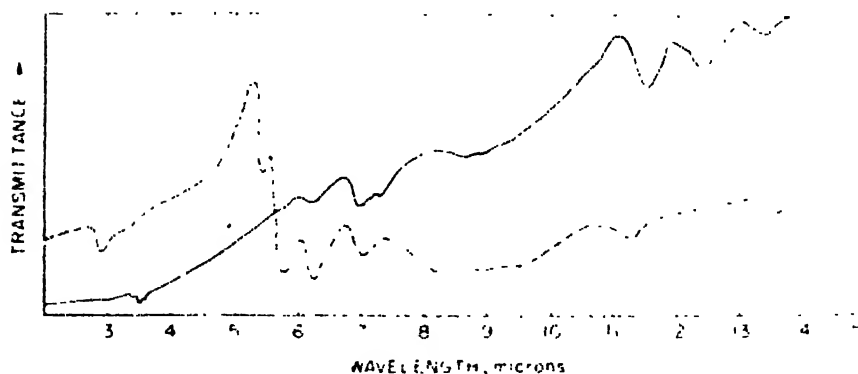


FIGURE 10-10. — *n*-Octacosane char, 450 C in inert atmosphere;
 --- *n*-Octacosane char, 450 C in air after preheat at
 350 C.

In order to check this conclusion, oxygen was introduced into the chars merely by forming the chars in the presence of air. Oxidative pyrolysis of anthracene and of *n*-octacosane produces spectra with strong coal-like 6.2μ bands (Figures 10-9 and 10-10). These are considered good indications that the 6.2μ band in these chars is mainly a chelated carbonyl band. The similarity of the spectra from anthracene and *n*-octacosane indicates that most of the absorption bands are due to oxygenated structures.

In an attempt to assign certain infrared absorption bands, particularly the aromatic bands, a completely deuterated paraffin was charred in the presence of oxygen.⁴² The aromatic bands did not appear in the 11 to 15μ

spectrum of the char; they were shifted to wavelengths beyond the rocksalt region, to 17μ .³⁹ Thus, these bands in the spectrum of coal are assignable to the vibrations of hydrogens on unsaturated carbon atoms because substitution of D for H on such structures shifts the absorption bands by a factor of about $\sqrt{2}$ to longer wavelengths. Broad absorption occurs at the 7μ CH bending region even though the deuterated char is essentially free of CH groups; this is an additional indication that the 6.9μ band in the coal spectrum is not due entirely to C-H vibrations. A band at 6.2μ is strong in the deuterated char and is assigned to an oxygen-containing group.

Additional labeling experiments are being carried out.⁴¹ For the further characterization of the 6.2μ band, an O^{18} compound will be used to produce a coal-like char. If the band is due to a chelated carbonyl structure, a measurable shift to longer wavelengths should be observed for the labeled char.

HIGH ENERGY EFFECTS

Photolysis

It is possible that photochemical changes occur in coals on being taken out of coal mines; no work on this possibility has been done. The photolysis of coals in the laboratory has been investigated by Bent and Brown.⁴ Irradiation of finely ground coal in water with a medium pressure mercury arc under an atmosphere of either nitrogen or air produced no change in the infrared spectrum. However, the benzene extract of the coal irradiated under the same conditions showed a strong bleaching effect and formation of a precipitate. Considerable oxidation takes place. If the benzene extract is irradiated in the absence of air under otherwise the same conditions, there is not nearly so much change. Thus a considerable photooxidation is indicated.

Photolysis with a mercury lamp of a suspension of coal in carbon tetrachloride also produced a decrease in CH absorption and incorporation of Cl into the coal structure.⁴

Nuclear Irradiation

Coals irradiated in various ways have been investigated by infrared. Generally infrared spectra have not shown any changes in solid coals produced by gamma, x-ray, or electron irradiation; changes in spectra have occurred for the most part only for neutron irradiation at high flux.⁴⁵ It is possible that infrared spectra might detect changes produced in solid coals by other modes of irradiation if the samples are investigated immediately. Gamma irradiation of a slurry of coal in CCl_4 has produced a large amount of a low molecular weight soluble substance.³² The infrared spec-

trum of this material obtained at the Bureau of Mines showed large changes, including production of intense ester bands and incorporation of CCl bonds; the reactions involved are not known.

The greatest changes in solid coal have been found for neutron irradiation at a flux of the order of 10^{19} neutrons/sq cm.⁴⁵ Five coals of various ranks from lignite to low volatile bituminous were investigated. Infrared spectra of the irradiated coals were more diffuse after the treatment, but specific absorption bands were unchanged, indicating that no appreciable changes in rank had occurred (Figure 10-11). Irradiation had least effect on the spectrum of the lignite (77.8% carbon) and the greatest effect on the high rank coals of about 90% carbon. The diffuseness of the spectra probably indicates an appreciable increase in molecular weights due to cross-linking reactions initiated by the irradiation.

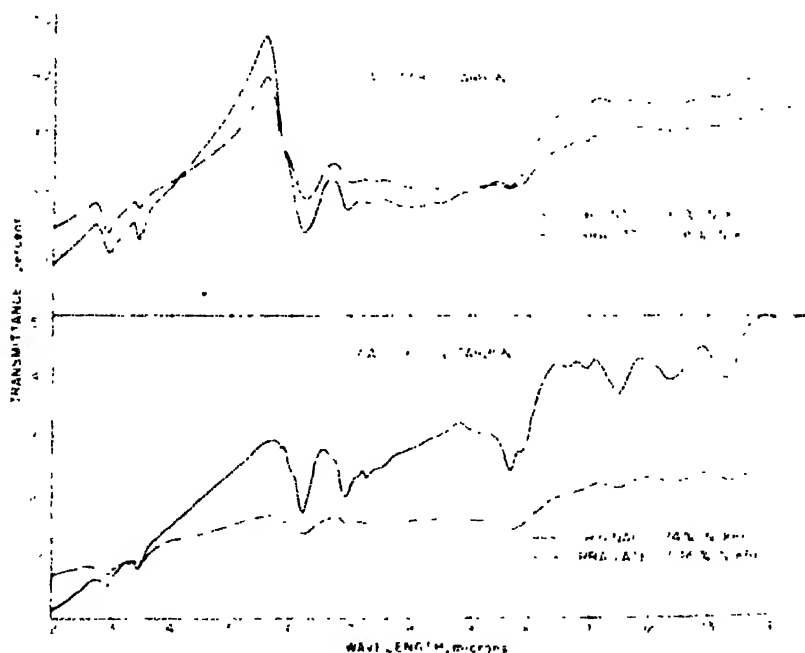


FIGURE 10-11. Effect of pile irradiation on the infrared spectra of coals containing 77.8 and 90.5% carbon.⁴⁵

Laser and Flash Irradiation

Experiments have also been carried out using flash irradiation and laser irradiation.⁹⁵ Drastic chemical and physical changes in the coal are produced by these two high energy processes. Low molecular weight gases

and a char are produced. The char is not easily characterized by infrared. It is similar in character to high temperature carbons which are known to be intractable.

Electrical Discharges

Considerable work is being done on coal subjected to electrical discharges such as corona, microwave, plasma-jet, spark, etc. Infrared has been of some help in the investigation of products of coal subjected to atomic species produced in a microwave plasma.¹⁰⁹ However, even with pure compounds, it has been difficult to characterize the solid residues obtained from electrical processes. Microwave^{109, 110} and negative glow¹⁰⁰ discharges in methane have produced solids that give broad-banded infrared spectra. Similar work has been carried out on electrical discharges in vapors of large hydrocarbons; it has been interesting to find that the infrared spectra of the products are similar.⁴¹ It appears that these electrical processes promote extensive decomposition of both small and large molecules followed by reassembling of the atoms or groups in random fashion. It is, however, possible from a study of the CH bands of these solids to establish the aliphatic and aromatic character of the product.

OTHER STUDIES

Microbiology

Work is being carried on in this field for several purposes: one of which is to search for a microorganism that will attack coal. This is a difficult problem because of the discovery that coal contains a very active antibiotic substance.⁹⁰ In associated studies infrared has been helpful in the identification of microbiological reaction products.

Sorbed Species on Coal

The sorption properties of coals have been studied extensively; the behavior of many molecules has been observed. The ability of H₂O and methanol to penetrate coal is especially intriguing, the infrared spectrum of coal with sorbed methanol is of interest, but the absorption intensity of coal itself makes it difficult to study sorbates by the usual transmission methods. Good spectra of methanol on coal have not yet been obtained.⁴¹ The method of attenuated total reflectance (ATR) holds considerable promise for sorption studies on coal. Pyridine on coal has been investigated by ATR and changes in the pyridine spectrum were clearly observed,⁴¹ as discussed in the next paragraph.

Charge-Transfer Complexing

The structure of coal may to some extent involve a combination of donor and acceptor molecules to form charge-transfer complexes. The high free-spin concentration shown by electron paramagnetic resonance is another indication that charge-transfer complexes may be involved. At present studies are being carried on in an attempt to evaluate the charge-transfer complexing capabilities of coal, either as a donor and/or an acceptor. It may be a fairly good acceptor substance, because of the complex which seems to be formed with pyridine. The spectrum of coal extract in pyridine is very similar to the infrared spectra of pyridine with other acceptor molecules.⁴¹

It is planned to investigate the possibility that coal may be a combination of unknown donor and acceptor molecules. The appreciable aromatic content of the coal would seem to signify the presence of appreciable amounts of donor molecules. The character of the acceptor molecule is difficult to estimate.

AROMATICITY

The aromaticity of coals, the types and sizes of aromatic structures in coal and coal derivatives have been intriguing questions. The first infrared work on aromaticity was done by Brown and Hirsch who demonstrated that ratios of aliphatic to aromatic hydrogens can be obtained from the CH str bands.¹⁶ After correcting for the presence of OH groups, the ultimate analysis of the coal was used to calculate the ratio of aliphatic to aromatic hydrogen atoms. Assuming that aliphatic carbon atoms are in CH₂ groups, the content of aliphatic carbon was calculated. Then the aromatic carbon content was obtained by difference. The results for 84% carbon coal is 72% aromatic carbon atoms, in single ring and, or polynuclear aromatic structures. The aromatic carbon content increases rapidly with increasing carbon content and reaches 92% aromatic carbons for coal of 93% carbon. The degree of substitution in the aromatic rings is apparently high for 84% carbon coal and the principal aromatic nuclei are probably 1-3 rings. In 93% carbon coals the substitution is less and the aromatic nuclei are larger, which is in keeping with the decreased aliphatic material in these coals.¹⁶

Hydrogen Distribution in Coal

The important study of hydrogen distribution has been continued by the recent work of Tschamler, deRuiter and Oth,^{82,83,103} Ladner and Stacey,^{69,70} and others.^{5,26,75,107} Present data on the distribution of hydrogen in coals between aromatic and aliphatic structures have been obtained from absorption area measurements and comparisons with model compound data.

Nuclear magnetic resonance data from soluble coal derivatives have indicated the appropriate infrared calibration data. Aromatic hydrogen distribution has been obtained by a detailed study of wavelengths and intensities of the long-wavelength aromatic bands. Assignments to specific types of aromatic structures have been made; the structures present apparently consist of isolated hydrogens, two adjacent hydrogens, and three and four adjacent hydrogens on single and polycondensed aromatic ring systems.

The near infrared work of deRuiter²³ has shown that the intensities of the second overtones of the aliphatic and aromatic CH str vibrations are nearly equal for many compounds. Accurate hydrogen distributions can therefore be calculated; the data are valid over a reasonably large range of aromaticities.

Recent results from combined infrared and nuclear magnetic resonance data on the distribution of aliphatic hydrogen into CH, CH₂, and CH₃ groups are indicating that the concentrations of CH₃ groups are surprisingly high. Evidence from the CH₃ band at 7.25 μ was formerly interpreted to mean that the methyl group content of coals was small,¹³ but appropriate calibration data are difficult to choose. Nuclear magnetic resonance data on soluble coal derivatives are now indicating that considerably higher amounts of methyl groups are present in coal. Through combined data present estimates for CH₃ and CH₂ groups are good, the content of CH groups is still in doubt, as is the question of the presence of aliphatic quaternary carbon atoms in coal.

Total and Polynuclear Aromaticity

The total aromaticity of coal and the polynuclear aromaticity of coal have been studied by various nonspectral methods.¹⁰⁵ The spectral methods applied to coal and coal derivatives include ultraviolet-visible,^{24 38,42 43,44,46,93 106} nuclear magnetic resonance,^{13 47} and mass spectrometry.⁹⁶ The initial work in the ultraviolet-visible spectrum^{38 43} interpreted the spectrum of a bituminous coal as indicating low polynuclear aromaticity,^{42,44} but this conclusion was controversial. More recent work has indicated that the original estimate of low polynuclear aromaticity could be correct.⁴⁶ Asphaltene from coal hydrogenation has also been assigned a low polynuclear aromaticity.^{42 47} Petroleum asphaltene is believed to have an even lower polynuclear aromaticity;¹⁵ or some large polynuclear aromatics are believed to be present.^{42,112}

CONCLUSIONS

Progress on the question of the structure of coal continues, and infrared spectroscopy is one of the chief contributors to this progress. It is possible to

formulate detailed structures satisfying the available evidence from many sources, on functional groups, aromatic nuclei, etc. The apparent repeatability of the coal unit or "molecule" promotes the attempt to speculate on structure and to meet the challenge to unravel the structure.

Two controversial facets of the coal "molecule" have been of particular interest to the writer: the questions of (1) five-membered rings and (2) polynuclear condensed aromatic structures. For many years the opinion that five-membered ring structures are plentiful in coal has been based on the many cyclopentyl and indan structures found in products from coal hydrogenation experiments.^{31 48,49 50 80 113 114} The temperatures involved in these experiments are low enough to permit the belief that the five-membered structures are present in the unreacted coal.

With regard to polynuclear condensed aromatics, the estimated average size for medium rank coals has decreased in the past decade from many rings down to the present 1-3 rings. Present evidence for the range of ring sizes and their concentrations seems overwhelming but it is unsafe to state that the present values are final. As suggested several years ago, polynuclear condensed aromatics are not needed to explain the color of coal, charge transfer complexes or unpaired electrons, presumably in free radicals, etc. do that.⁴³

The interested reader is referred to three recent books containing information on the structure of coal: Lowry,⁷² van Krevelen,¹⁰⁵ and Francis¹⁰⁶

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CHAPTER

11

Infrared in the Regulatory Agencies

*Jonas Carol and Alma L. Hayden**

INTRODUCTION

The enforcement of many federal, state and local laws depends on the investigations of analysts working in the various regulatory agencies. The problems confronting these workers are of an extremely diverse nature. Much of the work is routine and utilizes well established procedures. For example, the determination of the butter-fat content of milk is done many times daily in local health departments all over the country. At the other extreme, a chemist in the Federal Food and Drug Administration may find it necessary to separate, identify, and determine the many component steroids in a natural estrogenic hormone sample. Research work of this type, on the development of methods and related problems, is being done on an ever increasing scale. A tabulation of representative regulatory agencies and the nature of their work is shown in Table 11-1.

While there are no limits to the types of analytical problems encountered in the laboratories of these agencies, they must be solved bearing two facts firmly in mind. First, the results of analysis must be accurate and unequivocal. The findings of the analyst are frequently used in court action with personal liberty, or large financial losses at stake. An analytical error might result in grave injustice on one hand, or embarrassment to the Government, on the other. Second, the materials submitted to these laboratories, in many cases, are of an unknown nature. A few milligrams of a gray powder sent to the Federal Bureau of Investigation for identification could be one

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TABLE 11-1.

Agency	Nature of Laboratory Work
Alcohol and Tobacco Tax Unit U. S. Treasury Department	Analysis of narcotics, chiefly from illicit drug trade. Determination of alcohol for taxing purposes. Determination of age of liquors. Determination of alcohol denaturants.
Federal Bureau of Investigation U. S. Department of Justice	Identification of materials submitted to laboratory in connection with crime detection by the Federal Bureau of Investigation and associated police.
Food and Drug Administration U. S. Department of Health, Education, and Welfare	Analysis of foods, drugs, and cosmetics. Research on development of methods for these substances. Cooperation with other government agencies on analytical problems of a wide nature.
Bureau of Customs U. S. Treasury Department	Inspection and analysis of the great variety of substances offered for importation. Perfumes, plastics, fibers, gums, and drugs are typical examples.
Agriculture Research Service U. S. Department of Agriculture	Investigation into, and control of, composition of pesticides. Meat and poultry inspection.
Post Office Fraud Investigation U. S. Post Office Department	Analysis of many medicinal products, health foods, vitamins, etc., sent through the U. S. Mail.
State Food and Drug Administrations or their Equivalents	Laboratory work of the state organizations is similar to that of the Federal Food and Drug Administration.
City or Local Health Departments	Laboratories of some large cities have problems similar to state and federal food and drug laboratories. Most, however, are concerned with local problems, as water analysis, etc.

of a hundred thousand substances. The tranquilizer tablet sample being analyzed in a state laboratory has its identity established by label, but nothing is known of the tablet excipients and how they affect the accuracy of the procedure.

With the coming of commercial infrared spectrophotometric equipment in the late 1940's, it became possible to identify and estimate many sub-

stances with a speed and certainty far exceeding that of conventional chemical methods. The regulatory agencies were at first slow to take advantage of this most useful tool. No doubt the high cost of equipment was a major delaying factor. The Federal Food and Drug Administration first used infrared spectrophotometry to assay penicillin¹⁷ and to determine estrogenic hormones.^{4,8} The Federal Bureau of Investigation soon recognized the value of this technique in its crime detection work. Gradually, the directors of the regulatory agency laboratories began to recognize the advantages of infrared procedures. It was found that the original cost of equipment was a small factor compared with the saving of laboratory time. Of equal or greater importance was the solution of problems by infrared that had been insolvable previously.

Today infrared spectrophotometers have become a necessity in the laboratories of these agencies. The literature of analytical procedures using infrared spectrophotometry is voluminous. The United States Pharmacopeia XVI contains many infrared tests for identity, and several quantitative infrared methods. Any laboratory using the tests in these monographs must have infrared equipment. On several occasions the Federal Food and Drug Administration has used infrared analyses very successfully as court evidence.

No attempt will be made in this chapter to illustrate every problem in which infrared spectrophotometry is being used by regulatory agencies. Instead, a representative number of uses has been chosen to give the most complete coverage to this field possible from both a subject and technique point of view. These are actual examples in which infrared spectrophotometry has been used to solve a specific problem.

IDENTIFICATION OF UNKNOWN PHARMACEUTICALS

The analysis of a completely unknown pharmaceutical preparation is frequently required by many regulatory agencies. Usually the quantity of sample is limited, and occasionally no more than one tablet or capsule is available. A problem of this nature is a severe test of an analyst's ability. Great care must be exercised to avoid using the entire sample before its components are identified and estimated. Before the advent of spectrophotometry and chromatography only the most skilled and experienced worker would attempt such a task, and quite often he would fail to obtain conclusive results. With spectrophotometry and chromatography at his command, the modern analyst can attack this problem with every hope of success. The drug to be analyzed may contain a single active substance, or may contain a large number of compounds mixed with inert diluents. The analyst should first attempt to separate the active substances from the inert materials and

then, if necessary, to separate the active component compounds. This separation can best be accomplished by a systematic partitioning between immiscible solvents using neutral, acid, and basic conditions. This procedure first proposed by Fuller¹⁵ is still quite satisfactory, although newer solvents are now available. Closely related compounds cannot be separated by simple partitioning, but can be resolved by chromatography. The techniques described by Banes³ and Levine²³ have been extremely successful.

Once separation has been achieved, identification and estimation can best be made by ultraviolet and or infrared spectrophotometry. Each should be used where best suited. It should be emphasized, however, that the infrared spectrum of a substance, when matched with the spectrum of a known compound, provides positive means of identification. If the spectra differ, information relative to the structure of the unknown substance can still be ascertained. With this data ultimate identification is usually accomplished. Combinations of tests, such as melting point, index of refraction, and specific rotation, will indicate identity if the values found coincide with those of known substances. If these tests show differences, they yield few clues toward identification.

In the following cases infrared spectrophotometry provided the necessary proof of identity of the unknown substance.

Adulterated Hydrocortisone

A sample labeled "Hydrocortisone Tablets 20 mg" was received from a physician with the complaint that it failed to produce the desired physiological response in arthritic patients. Extraction of a weighed portion of the powdered sample produced a white crystalline residue equivalent to the declared amount of hormone. A potassium bromide disk was prepared of the residue since the adrenal cortex hormones are only slightly soluble in carbon disulfide or carbon tetrachloride. The infrared spectrum of the disk was similar to the spectrum of hydrocortisone, but differed from it in important details. In addition, the spectrum did not match that of any known adrenal cortex hormone. A paper chromatographic test, using formamide absorbed on the paper and a chloroform-methyl chloroform mobile solvent, produced two ultraviolet absorbing spots almost equal in intensity. The spots had R_f values equal to standards of hydrocortisone and Reichstein's Compound "S."

A weighed portion of the sample was chromatographed on a siliceous earth column containing formamide. Elution with benzene followed by chloroform yielded residues equivalent to 45 and 55% of total steroid content of the tablet. Infrared spectra of the two residues matched the spectra of Compound "S" and hydrocortisone exactly (Figure 11-1). This data combined with the paper chromatographic test gave conclusive

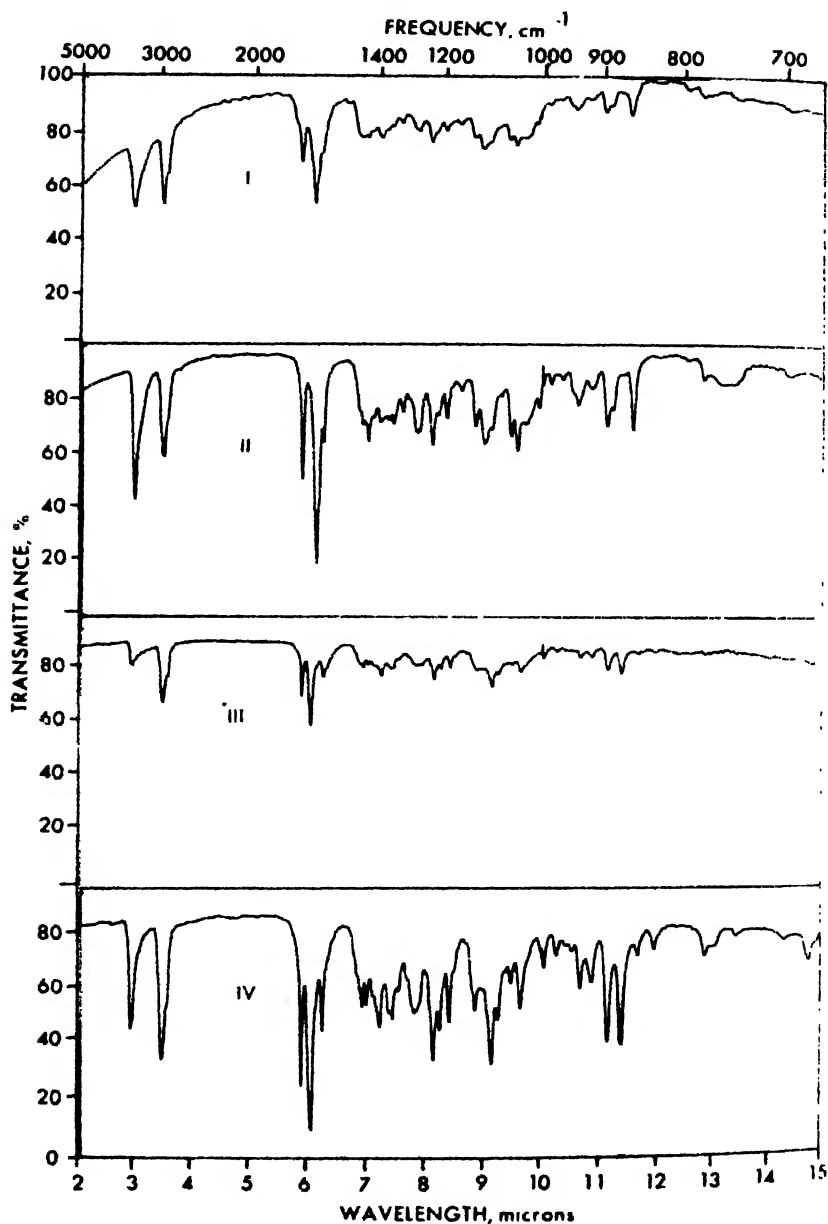
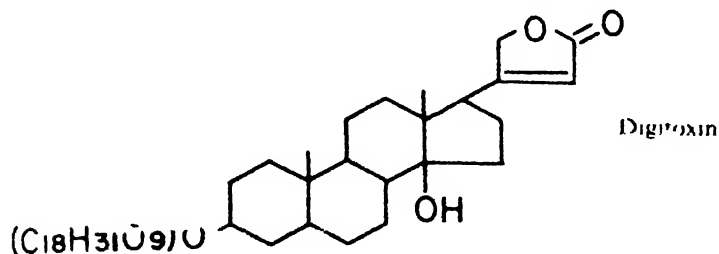


FIGURE 11-1. Infrared spectra of hydrocortisone (I) and 17-hydroxy-11-deoxycorticosterone (III) from column chromatography, and the corresponding standards (II) and (IV) as KBr disks.

proof of adulteration. As Reichstein's Compound "S" has no anti-arthritic properties, the tablets would produce only one-half of the therapeutic effect expected.

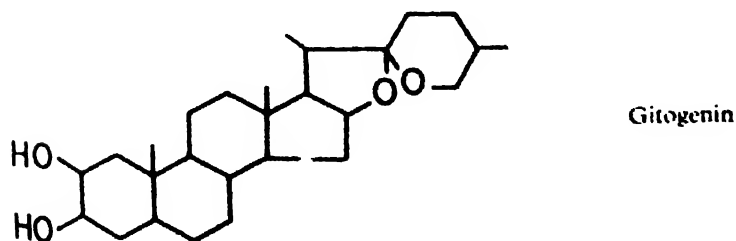
Contaminant in Digitoxin

An import sample of digitoxin, an important cardiac glycoside, assayed only 60% by the official U.S.P. XV procedure. In this assay, digitoxin is



separated from closely related glycosides by column partition chromatography. It is then estimated colorimetrically by the reaction of alkaline-pyrate solution with the butenolide side chain. Further analysis using the Keller-Kiliani test, which depends on the reaction with the digitoxose moiety, gave a comparable result. When the original sample was dissolved in alcohol, and its ultraviolet absorbance at 217m μ was compared with that of U.S.P. Reference Standard digitoxin, a result checking the first two was obtained. These analyses indicated the presence of about 40% of a non-glycosidal substance having little or no ultraviolet absorbance at 217m μ .

A reexamination of the effluent from the U.S.P. chromatographic separation revealed a white crystalline substance in the fore-run. This material, by weight, amounted to 40% of the sample. It had no ultraviolet absorption spectrum and gave no color with alkaline pyrate or Keller-Kiliani reagent. Since the residue was insoluble in carbon disulfide, its infrared spectrum was recorded using a potassium bromide disk. The spectrum had strong maxima in the regions where O-H and C-O-C absorb and had no carbonyl peaks. The spectrum suggested the presence of a sapogenin. Comparison of this spectrum with that of some of the common sapogenins produced a perfect match with that of gitogenin. The aglycone is a waste product



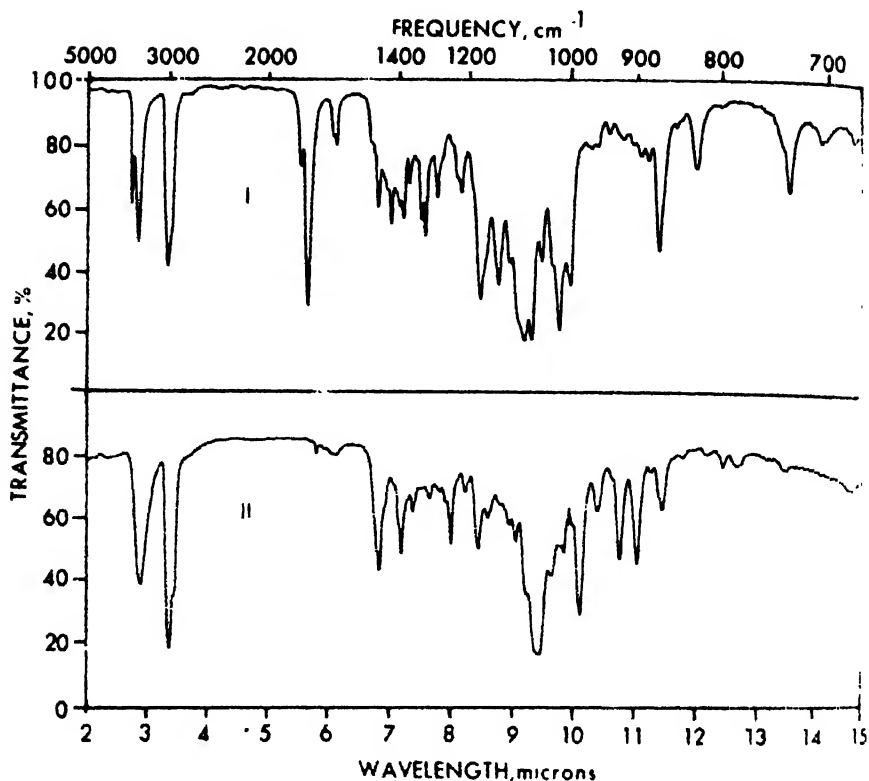


FIGURE 11-2. Infrared spectra of KBr disks of digitoxin (I) and gitogenin (II)

obtained in extraction of digitoxin from *Digitalis purpurea*. Investigation disclosed that an unscrupulous employee had been substituting this substance for part of the digitoxin in shipments of the bulk drug. He would then sell the withdrawn glycoside for his own gain. Needless to say, prompt legal action put a permanent end to this practice.

An Appetite Depressor

A consumer complaint sample consisted of a single capsule containing a mixture of colored granules typical of "timed release" pharmaceutical preparations. The sample had been sold, without prescription, as an appetite depressor. The consumer suspected the preparation might contain a drug that would be dangerous for use without a physician's supervision. Previous experience with this type of preparation suggested the possibility of several active constituents. A portion of the sample was ground, suspended in dilute sodium hydroxide solution and extracted with chloroform.

The chloroform solution was then extracted with dilute acid solution. The ultraviolet spectrum of the acid solution was that of amphetamine. The original alkaline solution was acidified, extracted with chloroform and the solvent was evaporated to dryness. A potassium bromide disk was prepared from a portion of the white crystalline residue. Its infrared spectrum was identical with that of phenobarbital. Neither of these two drugs can be legally sold without a prescription. Action was taken to prevent further violation by the pharmacist who made the sale.

Determination of Nitrate Esters

Nitroglycerin and the esters, pentaerythritol tetranitrate, erythritol tetranitrate and mannitol hexanitrate are extensively used for the treatment of certain heart diseases. These are life-saving drugs that must contain the labeled amount of active constituent to produce the desired physiological response. These drugs are routinely analyzed by chemists in the Food and Drug Administration.

The U.S.P. XVI³⁷ assay for nitroglycerin is based on the reduction of the nitrate groups to ammonia followed by distillation and titration with 0.01*N* acid. The procedure is nonspecific, time consuming, and not too precise. The other esters are usually analyzed by simple extraction with a suitable solvent, evaporation of the solvent, and weighing of the residue.³² A colorimetric procedure, depending on the formation of a yellow color with phenoldisulfonic acid is also used.⁴¹ These methods are convenient but are nonspecific. The gravimetric method is entirely unreliable if other soluble materials are present in the dosage form.

Rapid and specific quantitative spectrophotometric assays have been developed for these nitrate esters^{4, 7} as each has a distinct infrared spectrum. Nitroglycerin is extracted from powdered tablet samples with carbon disulfide and the extract is made to a definite volume containing about 3 mg/ml. The absorbance of this solution is measured at 7.90 μ , relative to a blank, in cells of 1 mm thickness. The absorbance of a standard solution* is measured in the same way and the quantity of nitroglycerin per tablet is calculated. Identity of the sample is established by comparing the spectra of sample and standard between 2 and 15 μ .

The other nitrates are not sufficiently soluble in carbon disulfide to produce satisfactory absorbance readings with cell thickness of 1 mm. Their solubility in chloroform is high enough for satisfactory readings. The nitroglycerin assay is modified to use chloroform as the extraction solvent and to measure the absorbances at 6.0 μ where chloroform is practically

*A convenient standard can be obtained as an absorbate on lactose containing about 10% nitroglycerin. These absorbates are quite stable. They can be standardized by the U. S. P. XVI assay.

transparent. As this solvent is not transparent throughout the 2 to 15 μ region, the qualitative test is made with a potassium bromide disk. The disk is prepared from the residue obtained by the evaporation of a portion of the chloroform extract. Although these nitrates are highly explosive, no difficulty is experienced in preparing the disks.

These compounds, especially mannitol hexanitate, are frequently dispensed in combination with other drugs such as phenobarbital, amorphylline and rutin. The latter two compounds are not extracted by chloroform from powdered samples and cause no interference in the analysis. Phenobarbital and other barbiturates can be separated easily by passing the extract through a siliceous earth column containing adsorbed trisodium phosphate. Infrared methods for each of these compounds in pharmaceuticals have been accepted by the A.O.A.C.* and the method for nitroglycerin in tablets is being considered to replace the present U.S.P. assay. These methods are being used routinely by the Food and Drug Administration because of their simplicity, accuracy, and specificity.

Analysis of Alkaloids

The analysis of alkaloids occupies an important place in the laboratory work of a number of agencies. These compounds are used in many pharmaceutical and drug preparations. A special class of alkaloids, narcotics, is under constant surveillance by the Internal Revenue Service.

The classical method of analysis of alkaloids involves precipitation of the base with an alkali, extraction of the base into an immiscible organic solvent, and recovery of the base by evaporation of the solvent. Final estimation is made either gravimetrically or by titration of the base with standard acid. A newer technique, applicable to many of these compounds, involves direct titration of the alkaloid salt in a nonaqueous medium. Since these assays are nonspecific, identification must be made separately. The most commonly used techniques are color tests, paper chromatography, and microscopic crystalline addition compounds of characteristic form.

By means of infrared spectrophotometry, highly specific analytical methods for these compounds have been developed giving qualitative and quantitative results in one operation. The analysis of atropine in pharmaceuticals⁶ is a typical procedure. The sample is extracted as in the classical method; the residue is dissolved in carbon disulfide and diluted to a volume of about 2 to 3 mg./ml. The absorbance spectrum is recorded, relative to a carbon disulfide blank, from 2 to 15 μ using 1 mm cells. Identification is made by comparison with the spectrum of a standard. Estimation is made from absorbance measurements at the 9.67 μ maximum. Any carbon disulfide

*Association of Official Agricultural Chemists.

soluble alkaloid such as hyoscyne, codeine, cocaine, nicotine, quinine and quinidine can be estimated by this simple procedure.

Occasionally it is necessary to analyze individual atropine tablets containing very small amounts of alkaloid (0.3 to 0.6 mg).¹ Determinations are made following the procedure used for macro samples except that the alkaloidal residue is dissolved in 0.5 to 1.0 ml of carbon disulfide and the baseline absorbance of the sample and standard solutions are measured at 9.67μ using $5\times$ ordinate expansion¹⁰ (Figure 11-3). Analyses of commercial tablet samples showed excellent recoveries based on labeled declarations (Table 11-2).

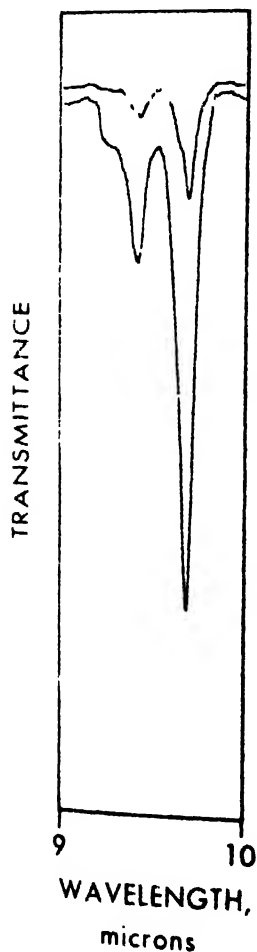


FIGURE 11-3 The 9.67μ band of atropine under 1X and 5X ordinate expansion of 0.4 mg/ml CS_2 in 1-mm NaCl cells.

TABLE 11-2. RECOVERIES OF ATROPINE SULFATE TABLETS

Sample	Declared/tablet (mg)	Found	
		mg/tablet	per cent
1	0.324	0.316	97.5
	0.324	0.322	99.4
2	0.432	0.416	96.3
	0.432	0.416	96.5
3	0.648	0.670	103.4
	0.648	0.701	108.2

Atropine, hyoscyamine (*dl*-atropine), and the closely related alkaloid hyoscyne are frequently dispensed, together with barbiturates, as components of medicinal preparations. In these combinations, hyoscyne comprises no more than 10% of the total alkaloids. The infrared absorption spectra (in solution) of atropine and hyoscyamine are identical. The spectrum of hyoscyne has marked differences, but analysis of a two-component system is not feasible when one is a minor component.

Mixtures of hyoscyne and atropine have been separated by an ingenious chromatographic procedure,²⁴ based on slight differences in alkalinity

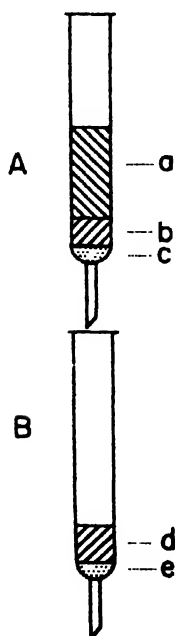


FIGURE 11-4. Columns, containing 1*N* NaHCO₃ (a), 1*M* K₂PO₄ (b), and pH 6.3 McIlvaine buffer (d) on Celite, used in analysis of atropine and hyoscyne mixtures. (c) and (e) are glass wool.

of the two bases. Final estimation of each compound is made by infrared.¹ Two columns are prepared as illustrated in Figure 11-4 and are mounted so that the effluent from A passes through B and is collected in a suitable container. One hundred ml of washed benzene is passed through each tube. Barbiturates are trapped in the phosphate layer of column A, atropine is trapped in column B, and hyoscine passes through and is collected. The columns are separated and atropine is eluted from column B with 100 ml of chloroform. Each fraction is evaporated to dryness and the two alkaloid residues are dissolved in carbon disulfide and determined as previously described. The atropine absorbance measurement is made at 9.67μ and the hyoscine measurement made at 11.17μ . In most cases, atropine is present in sufficient quantities to allow the use of the macro technique. Hyoscine must

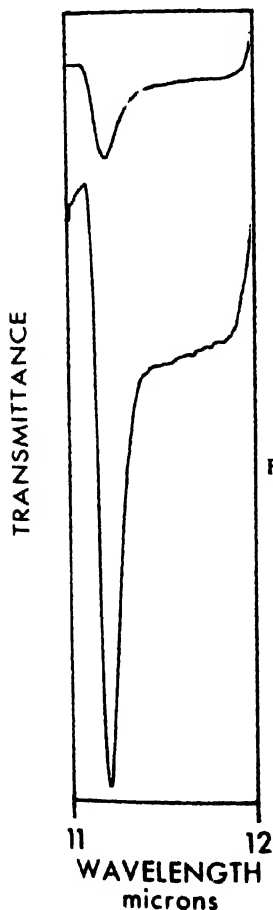


FIGURE 11-5. The 11.17μ band of hyoscine under 1X and 5X expansion at 1.5 mg/ml CS_2 in 3-mm NaCl cells.

be determined with ordinate expansion (Figure 11-5). Two analyses made with synthetic mixtures (Table 11-3) show very good recoveries for this type of sample.

TABLE 11-3. ANALYSES OF SYNTHETIC MIXTURES

Sample Number	Ingredients	Added (mg)	Found	
			mg	per cent
1	Atropine sulfate	4.770	4.746	99.5
	+ Hyoscine hydrobromide	0.364	0.320	87.8
2	Atropine sulfate	4.800	4.896	102.0
	+ Hyoscine hydrobromide	0.360	0.346	96.2
	Atropine sulfate	4.800	4.896	102.0
	+ Hyoscine hydrobromide	0.360	0.347	96.4

Many alkaloids, however, are not sufficiently soluble in carbon disulfide (or other suitable solvents) to use this approach. For these, the potassium bromide disk technique offers the next best sample handling procedure. Much has been written, both pro and con, regarding the reliability of this technique. The recent work of Hayden and Sammul²⁰ in this field shows that quite accurate and reproducible results can be obtained providing careful attention to details is observed.

A major activity of the laboratory of the Alcohol and Tobacco Tax Unit of the Internal Revenue Service is the analysis of narcotics sold through illicit channels. These analyses must be unequivocal since they are frequently the basis of legal action. Analysis also must often be made on very small samples. Infrared spectrophotometry is ideal for this work. Two papers by Pro^{18,19} report the determinations of methadon and meperidine, synthetic narcotics, using procedures similar to that described above for atropine.

The analysis of cocaine hydrochloride in the presence of procaine and/or tetracaine hydrochloride constitutes a more difficult problem. The latter two compounds are common diluents of illicit cocaine samples. Pro *et al.*⁴⁰ determined these mixtures by ultraviolet spectrophotometry, and made a positive identification of cocaine hydrochloride in mixtures without separation by infrared spectrophotometry. Also, in this agency, infrared spectrophotometry has replaced all other tests for the identification of the many morphine and heroin samples routinely collected by their agents.

Determination of Estrogenic Hormones in Complex Mixtures

Soon after the isolation of estrone in 1929, estrogenic hormones were being prescribed for certain hormone deficiencies. Zondek, in 1933,⁴⁷ discovered an abundant source for these substances; pregnant mares' urine. Although synthetically prepared steroids are now available, the naturally occurring compounds are still widely used. These estrogenic substances are a complex mixture of at least nine closely related compounds varying markedly in therapeutic activity (Figure 11-6).

Early analytical methods for these hormone preparations were biological assays using mice or rats as test animals. These methods definitely measured estrogenic activity, but suffered serious weaknesses; they were time consuming, costly, and lacked precision. First attempts at chemical assays only measured total estrogens and gave no indication of potency. A procedure suitable for use in the regulatory agencies must accurately and rapidly estimate each of the physiologically active estrogens present in a pharmaceutical preparation. These drugs are usually labeled to indicate either the weight or the international units of total estrogens per volume or tablet (capsule). The latter designation is not entirely correct as only estrone has been defined in that manner. The assumption is made, however, that estrone and mixed estrogens have essentially the same potency. This assumption is true only if the mixture is predominantly estrone.

By the early 1940's, before suitable analytical methods were available, the adulteration and misbranding of estrogens were common. Two general types of violations were the substitution of estradiol-17 β for mixed estrogens, and significant shortages of total estrogens. The bioassays used detected the overall shortages, but could not distinguish between the various estrogens. Estradiol-17 β exhibits ten times the potency of estrone when tested biologically. Unscrupulous manufacturers soon discovered this fact and began selling preparations labeled as natural estrogens but containing only one tenth the quantity of estradiol-17 β . This substitution was of serious nature because the two hormones have about equal therapeutic activity in humans, and, consequently, such an adulterated product would have but 10% of the required potency. Infrared spectrophotometry appeared to be the one technique capable of determining the complex hormone mixtures obtained from pregnant mares' urine. Furchgott *et al.*¹⁶ had obtained the infrared spectra of some of the estrogens using films and all exhibited differences. Workers in other fields had made quantitative infrared analyses of multi-component mixtures without previous separations. In the case of the estrogens it was possible to separate them from impurities by means of immiscible solvents. A further separation into ketonic and nonketonic fractions was made with Girard's Reagent T. The estrogens are almost

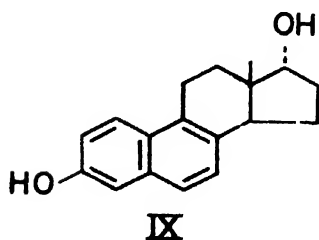
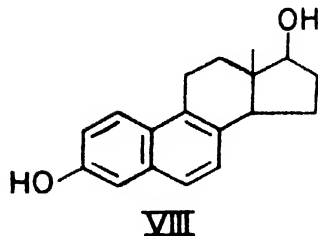
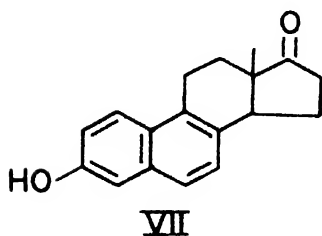
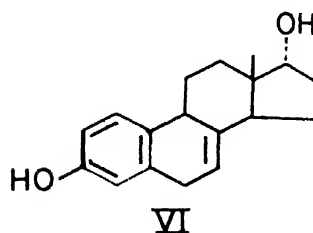
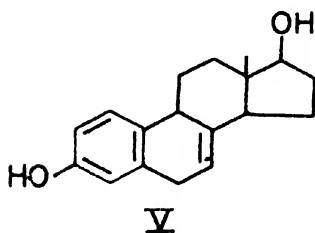
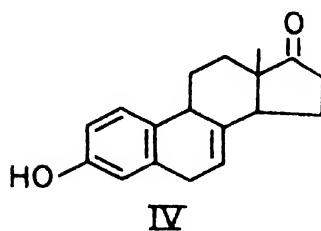
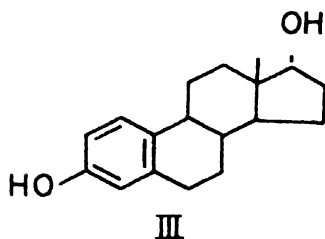
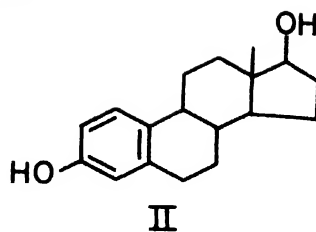
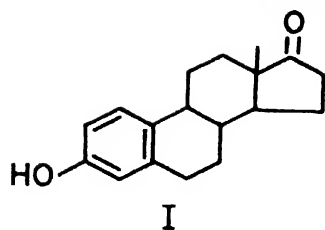


FIGURE 11-6. Structures of the naturally occurring estrogens, estrone (I), estradiol-17 β (II), estradiol-17 α (III), equilin (IV), dihydroequilin-17 β (V), dihydroequilin-17 α (VI), equilenin (VII), dihydroequilenin-17 β (VIII), and dihydroequilenin-17 α (IX).

insoluble in carbon disulfide and carbon tetrachloride, the best infrared solvents. However, they are readily converted quantitatively to their benzene sulfonyl esters. These esters are sufficiently soluble in carbon disulfide to produce satisfactory absorbances when measurements are made in cells of 1 mm thickness (Figure 11-7). The three ketones, estrone, equilin, and equi-

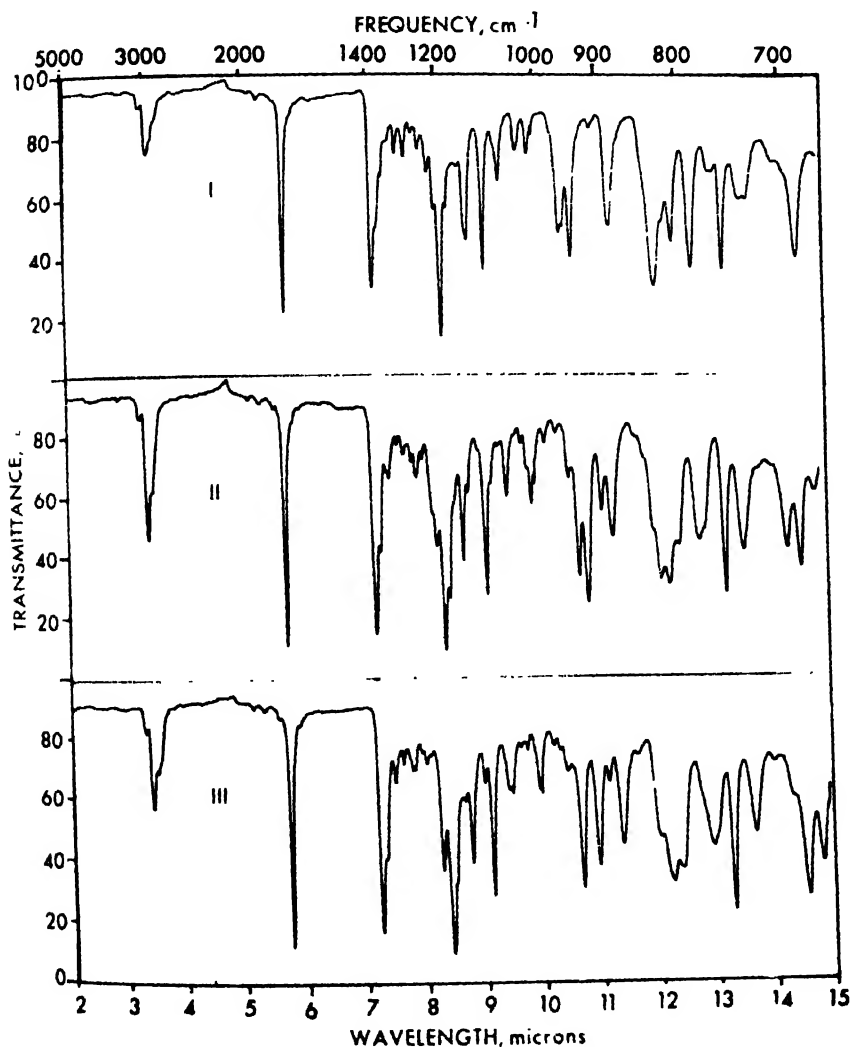


FIGURE 11-7. Infrared spectra of the benzene sulfonyl esters of equilenin (I) estrone (II) and equilin (III) in CS_2 .

lenin are determined by absorbance measurements made at 10.88, 10.96, and 10.45 μ , respectively. Calculations were made by means of approximation

Estradiol-17 β , as its benzene sulfonyl ester, has an extremely characteristic spectrum with a peak at 10.10 μ . Base-line measurements at this wavelength

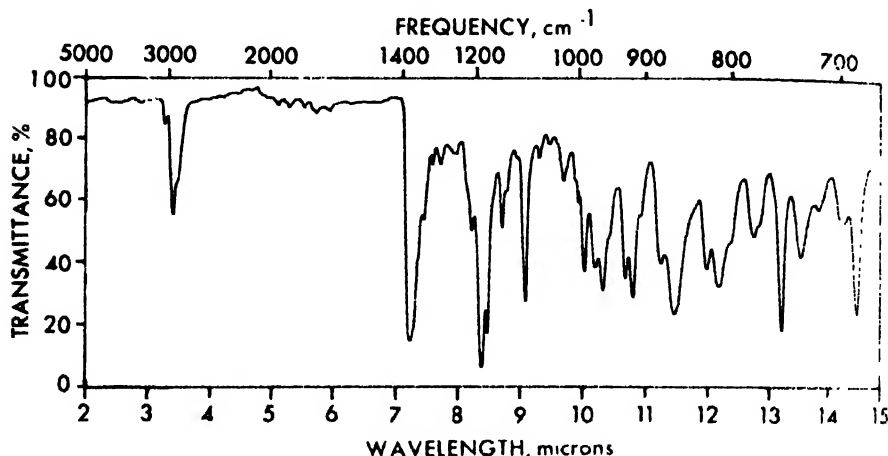


FIGURE 11-8. Infrared spectrum of the benzene sulfonyl ester of estradiol-17 β in CS₂.

give quite accurate results for this active diol. If a determination of each of the diols is needed, a simple chromatographic separation prior to infrared analysis is necessary.

Infrared analysis of the estrogens from known samples of pregnant mares' urine established the facts that the ketosteroid fraction always exceeded 85% of total estrogens, that the estradiol-17 β content of fresh urine did not exceed 1% of the total hormone content, and the proportion of the three ketosteroids varied with the term of the mare pregnancy but that estrone was always the major component and equilenin the minor one. These facts were used as the basis for judgement in determining compliance with labeled claims for these estrogens.

Pesticides

The widespread use of organic pesticides on food crops has necessitated general procedures for the separation, determination, and identification of these substances in plant and animal fat extracts. This problem is magnified by the need for rapid analysis of perishables and for the detection of degradation products which may form on standing. State and federal laws limit the amount of these substances that may be present in foods and food products.

As a result, the separation and detection of organic pesticides must be rapid, sensitive, and precise.

In general, the determination of organic pesticides involves the separation from plant or animal sources by extraction or elution with a suitable solvent. The use of paper³⁰ and column chromatography²⁹ has greatly improved the isolation of pesticides from excipients. The chromatographic separations are more efficient and less time consuming than classical shake-out procedures. Therefore, the possibility of breakdown of these compounds during analysis is reduced.

Until recently, analyses of these isolated pesticides were made by weighing the crystalline residues, by ultraviolet or visible spectrophotometry, by titration, or by other chemical means.³⁴ These methods were nonspecific and assumed the absence of contaminants with similar functional groups.

In recent years, several reports have been made on the determination of pesticides by infrared spectrophotometry. The absorption bands, due to out-of-plane deformations which occur in the 1200 to 650 cm^{-1} region are very useful for analyses of these compounds. The very high intensity of these bands makes them particularly well suited for quantitative work. The use of bands in the "fingerprint" region reduces the interference due to breakdown products with the same functional groups as the pesticides.

With appropriate preliminary procedures, infrared spectroscopy has been used to analyze residues of organic phosphate pesticide;²⁷ to verify the stability of formulations;¹⁶ and to follow various chemical changes.²⁵ Some examples of these applications are given below:

(1) The alpha, beta, gamma, delta, and epsilon isomers of hexachlorocyclohexane (benzene hexachloride) are not differentiated by the chromatographic separation on silicic acid columns. However, the combination of infrared spectrophotometry with column chromatography is an official procedure³⁵ for determining these isomers in the presence of each other. Solutions of the column eluate in carbon disulfide are read at 12.58, 13.46, 14.53, 13.22, and 13.96 μ . Using working or calibration curves for each isomer at each wavelength, the corrected absorbance and amount of each component in the mixture are calculated.

(2) The ready solubility of DDT in carbon disulfide has made possible the determination of this compound in dust samples.²¹ The method involves the extraction of DDT from the dusts with carbon disulfide. The dried extract is measured between 8.5 and 10.5 μ . The calculations are based on comparisons of the base-line absorbance for sample and standard at 9.83 μ . Average results within 2% of the known amount have been reported.

(3) The determination of malathion in powders, dusts, and emulsions⁴⁶ represents the solution to one problem often encountered in infrared spectrophotometry. The infrared transparent solvents were inefficient for

the extraction and spectroscopy of this compound. Preliminary investigation revealed acetonitrile to be a satisfactory extractant and to be transparent in the 12.0μ region. The absorbance of sample and standard were measured between 11.0 and 13.0μ and the malathion was determined by a modified base-line procedure. The average results agreed within 4% with the amounts known to be present.

(4) Some of the phosphate pesticides, after suitable separation from plants, have been determined by their infrared spectra in carbon disulfide.²⁷ As little as 0.75 ppm of some pesticides were separated and identified. The spectra of these compounds are distinctive and the determination and structural correlations have been made.

Gums

A variety of gums are used as stabilizers, and as thickening and binding agents in commercial food, drug, and cosmetic products. The use of these compounds has improved the appearance and public acceptance of old products and has aided in the development of new products. However, the presence of these agents has complicated the analyses of the active components. A need exists for analytical methods for detecting and identifying gums in the presence or absence of active ingredients.

One of the major problems in the analysis of gums is the difficulty encountered in separating these compounds from foods, drugs, and cosmetics. Several methods of isolation have been described.^{22,44} In general, the product is defatted with ether, benzene, or some similar solvent. The proteins are precipitated with trichloroacetic acid or other deproteinizing agents. The gum is then precipitated from aqueous solution with alcohol.

The detection and identification of these gums, until recently, presented further complication in these analyses. Official methods of analysis³⁶ for foods, drugs, and cosmetics have relied on chemical tests for sugars after hydrolysis of the gums and on precipitation or color tests in the presence of certain reagents. Gums in soft curd cheese were hydrolyzed and the resulting sugars detected with Benedict's solution. Gums in salad dressing were precipitated with basic lead acetate reagent. Gums in drugs were detected by color tests with chlorzinciodide, alcoholic iodine, dyes, and sulfuric acid. Ewart and Chapman¹⁴ used a combination of solubility and chemical tests to detect the precipitated gums. While these methods were useful, they were nonspecific. Other components having similar solubilities, or the presence of sugars from other sources, sometimes resulted in erroneous identifications.

In 1952, Newburger and co-workers³⁴ described a technique for obtaining the infrared spectra of films of water-soluble gums. In this method, a film of the gum is deposited from aqueous solution onto a water-repellent glass

plate. The latter is prepared by coating a glass plate with an organo-silicon compound. The excess silicone material is removed with lens paper and the plate is washed with water and dried. An aqueous solution of the gum is deposited on the water-repellent plate. The plate is heated and the resulting film is removed with forceps, razor blade or some other similar device. The film is dried at 105°C for about 30 min. The dried film is placed between two sodium chloride plates and mounted in an infrared spectrophotometer. The infrared spectrum against air is obtained in the region 2 to 15 μ .

The spectra of the fifteen gums, methylcellulose, Irish moss, tragacanth, karaya, gelatin, potato starch, algin, quince seed, locust bean, guar flour, arabic, ghatti, pectin, agar, and sodium carboxymethylcellulose were published. Although there was general similarity among the spectra, there were sufficient differences to characterize the gums. The reported spectra were used to identify gums isolated from foods, drugs, and cosmetics. Using this method, algin from cottage cheese, arabic and sodium carboxymethylcellulose from ice cream, and tragacanth from French dressing were identified. In addition, karaya gum was found in wave set powders, and Irish moss was identified in suntan lotions.

McNulty²⁸ recently combined improved separation methods and infrared spectroscopy of deposited films in the identification of gums in frozen desserts. The usefulness of this technique is readily apparent. It represents a major improvement over other physical and chemical means of analysis.

Adulterated Horseradish

The versatility of infrared spectrophotometry in solving difficult and unusual analytical problems is illustrated by a case of parsnip in prepared horseradish. Horseradish root fluctuates quite widely in price and is sometimes quite expensive. Some manufacturers would adulterate prepared horseradish with certain cheap and bland roots such as turnips and parsnips, obtaining the required pungency through the addition of oil of mustard (allylisothiocyanate).

A series of samples of prepared horseradish collected by Food and Drug inspectors was analyzed microscopically and found to contain significant amounts of parsnip root cells. Estimation of the amount of adulteration ran from 30 to 50%. If the presence of added synthetic allylisothiocyanate could be shown, added proof of adulteration could be established. However, the infrared spectrum of the synthetic material, and the oil distilled from authentic horseradish root were found to be identical. Fortunately, the infrared spectrum of the oil steam-distilled from authentic parsnip roots was quite characteristic, and entirely different from that obtained from turnips, onions, radishes or beets. It was quite different from the spectrum of allylisothiocyanate.⁹ The spectrum of the oil steam-distilled from the samples

showing microscopic evidence of adulteration had peaks common to both synthetic mustard oil and parsnips. Approximate calculations of the amount of parsnips present were made from the intensities of the peaks at 4.75 and 6.65 μ . The results of these calculations were surprisingly close to those made microscopically. At a court case, in which the seizure of these horseradish samples was being contested by the manufacturers, the infrared evidence carried great weight with the judge. The verdict was in favor of the government.

Analysis of Nail Lacquers

The laboratories of federal and state Food and Drug units are frequently called upon to analyze cosmetic preparations in connection with allergy investigations. The analysis of these products by conventional chemical methods is both tedious and uncertain due to difficulties of separation and identification. With the advent of infrared spectrophotometry, much progress has been possible in this field.

Early work in this area was stimulated by an infrared analysis of a finger nail "undercoat" preparation. This product had been developed to produce a smooth and binding foundation for nail lacquer. Soon after its appearance on the market, many complaints were received from women whose nails became blackened. In a few cases, loss of nails was reported.

Films of the sample were prepared by "painting" the sample on a sodium chloride plate and allowing the solvent to evaporate. Traces of solvent were removed in a vacuum. Spectra of these films were recorded from 2 to 15 μ and compared with the curves obtained from various resins, plasticizers and synthetic rubber, etc. It was noted that the sample film had a number of maxima at wavelengths identical with those of phenolformaldehyde polymer and synthetic rubber, butadiene-acrylonitrile polymer. From a consideration of the relative intensities of these maxima, it was possible to prepare a mixture of these two products having a spectrum almost identical with that of the sample film. Further investigation showed that the phenolic resin was responsible for the allergic reaction, and sale of this preparation was discontinued.

This investigation gave impetus to the development of a systematic scheme of analysis of nail lacquers based on infrared tests for identity.

Newburger³³ prepared mixtures of nitrocellulose, *n*-butyl phthalate and aryl sulfonamide-formaldehyde resin. These materials are common non-volatile constituents of colorless nail lacquer. An extraction technique using immiscible solvents separated the compounds into fractions. These were evaporated to dryness, weighed, and the residues were identified by infrared spectrophotometry. Each residue gave a distinctive spectrum. This procedure now is routinely used for the analysis of these products.

Coal Tar Colors

The certification of coal tar colors for use in foods, drugs, and cosmetics is an important function of the Federal Food and Drug Administration. A permitted color must have been found safe for use by pharmacological tests. Many of these dyes are complex substances: mixtures of closely related isomers instead of single compounds. The possibility always exists that changes in manufacturing methods may change the proportion of isomers in the product, or introduce entirely new ones.

Investigations into the exact composition of these substances made little headway until infrared spectrophotometry became available. Then the complexity and variability of these products became apparent. This knowledge posed two serious questions: (1) What are the toxicities of the various isomers, and (2) are the presently available colors as harmless as those on which the original biological tests were made? A wide-scale research project, in which infrared spectrophotometry played a very important role, was instituted to answer these questions. This research has been directed toward: (1) an evaluation of the purity of commercial certifiable colors, (2) a study of the intermediates of certain colors in order to learn the conditions controlling isomer formation, and (3) the synthesis of pure color compounds for use in pharmacological evaluations of toxicity.

The work of Dolinsky and Jones¹² was undertaken to obtain a file of spectra of the unsulfonated monoazo dyes and related compounds. The spectra of thirty-one compounds were recorded from 2 to 15 μ . This investigation revealed many cases of unsuspected contamination. These were detected by the presence of strong absorption bands in regions of the spectrum where none should appear, i. e., a strong 3.0 μ peak in the spectrum of a substance lacking O—H or N—H groups.

Dolinsky and co-workers¹³ investigated the isomers formed in the synthesis of pseudocumidine, 1-amino-2,4,5-trimethylbenzene, an intermediate in the manufacture of FD&C Red No. 1. Commercial pseudocumidine contains appreciable amounts of other hydrocarbons such as three isomeric ethyltoluenes and hemimellitene, 1,2,3-trimethylbenzene. When the commercial product is mononitrated and reduced to the amino-compound, a mixture of products results. Each of these amines was made synthetically and its infrared spectrum determined. From this data it was possible to estimate the amount of each amine present in the product made from commercial pseudocumidine.

Graichen and Molitor¹⁴, using chromatographic, ultraviolet, and infrared techniques, examined twenty commercial samples of D&C Orange No. 5 (4,5-dibromofluorescein). Prior to analysis it was necessary to prepare each of the suspected contaminants and determine their infrared spectrum. The results of their analyses (Table 11-4), show the wide variation in composition of material from different manufacturers.

TABLE 11-4. COLOR ANALYSES OF COMMERCIAL SAMPLES OF D & C ORANGE No. 5

Manufacturer	Fluorescein (%)	4-Bromofluorescein (%)	2,4- and 2,5-Dibromofluoresceins (%)	4,5-Dibromofluorescein (%)	2,4,5-Tri-bromofluorescein (%)	2,4,5,7-Tet-bromofluorescein (%)	Unidentified Colors (Estimated %)
A	Trace	24	3	56	8	7	2
	1	26	2	55	8	7	1
	Trace	21	2	58	8	8	2
	1	24	3	56	8	7	2
B	1	18	1	51	10	16	3
	2	21	1	43	11	21	2
	1	20	1	50	10	15	2
	1	14	1	56	10	15	3
	1	23	2	56	9	9	1
C	1	22	2	59	9	6	2
	Trace	20	2	61	8	7	2
	Trace	19	2	61	7	8	2
	1	8	0	82	4	5	0
E	Trace	18	2	62	9	7	2
	1	25	3	55	8	7	2
F	3	29	0	55	3	10	1
	2	25	0	57	4	12	1
	Trace	1	0	94	5	Trace	0
	1	0	0	86	10	3	Trace
	0	0	0	91	7	1	Trace

USE OF INFRARED BY THE FEDERAL BUREAU OF INVESTIGATION

The facilities of the F.B.I. laboratories are available, without charge, to all authorized law enforcement agencies throughout the country. Consequently specimens of evidence are examined by the laboratory in connection with every type of criminal case. Many of these specimens are minute quantities of totally unknown substances. The laboratories must endeavor to identify these materials or prove their origin. For this work infrared spectrophotometry has proved to be a valuable tool. Samples of drugs, poisons, plastics, rubber products, waxes, and petroleum products are but a few of the substances that have been analyzed by this technique.

The F.B.I. laboratories' aid was enlisted to help find the cause of death of a young child. She had been the third child of a family to die under mysterious circumstances. Steam-distillation of the child's organs yielded a very small amount of an oily liquid. The infrared spectrum of this oil was quickly matched with that of methyl salicylate, a highly toxic internal poison.

In another case, police investigating a series of "safe-crackings" found a hidden sack of heavy wrecking tools. The tools were dusted with a fluorescent powder. In a subsequent safe robbery, fluorescent material was found at points of entry. Four suspects when apprehended had clothing and money showing fluorescence. Only very small amounts of powder could be recovered from the safe, clothing and money, but adequate infrared spectra were obtained. These spectra were identical with the spectrum of the original fluorescent powder. Faced with this conclusive evidence, the four suspects pleaded guilty.

In an armed robbery case an infrared spectrophotometric examination played an outstanding role. The robber had abandoned a home-made gun at the scene of the crime. The varnish on the gun's handle was compared by infrared with varnish in a can at a suspect's home. The absorption spectra were identical. This information was an important contribution toward conviction of the accused.

DEVELOPMENT AND APPLICATION OF NEW TECHNIQUES

The laboratories of the regulatory agencies are constantly confronted with new problems. The development of new products, and the passage of new laws have presented these laboratories with increasingly difficult tasks. An active search for new methods and techniques is a necessity. Each year brings many new products, e.g., food additives, nutritional adjuncts, complex pharmaceuticals, and highly toxic organic pesticides. Often these materials occur in amounts less than 500 mcg in mixture with organic and in-

organic components. The analyses of such samples by macro methods require prohibitively large samples. In addition, extensive purification from large amounts of interfering materials is necessary. The need for methods of isolation and determination of such small amounts is apparent.

In recent years, several reports have been made on the infrared spectra of microgram quantities of liquids, solutions, and solids. Using these procedures there is little difficulty in analyzing 100 mcg and less of pure compounds and synthetically prepared mixtures. By modifying the sample purification to reduce sample or solvent impurities, these methods can be adapted to commercial and biological samples.

The analyses of micro amounts may require modifications of existing macro procedures or the development of new methods. Substances which are soluble in the infrared transparent solvents are dissolved in the minimum volume of solvent required to fill the cells. The spectrum of solutions of 1 mg/ml or greater may be obtained in the usual manner with microcells, 1 to 3 mm in thickness. For low concentrations of solutions and of solids intensification of the infrared beam²⁶ or of the spectrum¹⁰ is required. The afore-mentioned examples of atropine and hyoscyne are representative of the latter approach.

The differentiation of vitamin D₂ and D₃ by Morris and co-workers¹ represents a novel approach to infrared spectrophotometry. Structurally these compounds differ by a methyl group at the C-24 position and a double bond between C-22 and C-23 in the vitamin D₂ molecule. In mammals, both forms are useful in the prevention of rickets. However, vitamin D₂ is about 1/100th as effective as vitamin D₃ in poultry. Therefore, a specific method was needed for the control of vitamin D poultry feed supplements. The infrared spectrum of vitamin D₂ shows absorption at 10.3 and 10.4 μ , whereas vitamin D₃ has only the band at 10.4 μ . Using this difference, the pure substances were differentiated by their spectra. Percentage composition of mixtures of the two forms were quantitatively estimated by a ratio of absorbance differences at 10.3, 10.4, and 10.5 μ . Using a 3 mm microcell, a useful spectrum was obtained of 250 mcg of the pure vitamins. Poultry feed supplements contain background material which was not removed by chromatography. The authors used differential spectrophotometry where a known amount of vitamin D₂ or D₃ was placed in the reference cell to neutralize the vitamin D absorption in the sample. The amount of vitamin D₂ or D₃ required in the reference cell indicated the form and amount of vitamin D in the sample.

Of the several known procedures for obtaining spectra of solids, the potassium bromide method is the most easily adapted to qualitative and quantitative analysis. The advantages of this method are greatly emphasized in the study of micro amounts of solids. In general, modifications of the

procedures of Schiedt⁴² and Stimson⁴³ are followed. The solid is dispersed in potassium bromide or other alkali halides. The resulting mixtures are pressed into glass-like disks or plates under external force. With an awareness of the possibility of anomalous spectra formation,² this method has been applied to a variety of compounds. Several regulatory agencies have used this method routinely in the qualitative identification of cosmetic, antibiotic, food, narcotic, pesticide, and pharmaceutical samples. Recently, reports on the usefulness of this tool in quantitative analyses have been made. In addition to other compounds, quantitative procedures have been developed for pharmaceuticals of varied origin. Cortisone, hydrocortisone, ethisterone, caffeine, phenacetin, warfarin, and meprohamate have been analyzed.²⁰

As a general procedure, the active component is separated from tablet excipients on a chromatographic column or by classical shake-out techniques. After evaporation of the extracting solvent, the residue is dissolved in a volatile solvent. Aliquots of the solution may be analyzed by hand-grinding with potassium bromide for five to ten minutes during which time the solvent evaporates. Alternatively, residues of aliquots may be ground with potassium bromide in a mechanical vibrator for an accurately measured time. The ground mixtures are dried, pressed into disks, heated at 105°C for 15 to 30 min, cooled to room temperature and observed in the region 2 to 15 μ . The spectra are compared with those of disks of the standard prepared in the same manner.

Quantitative determinations are made from a modified Beer-Lambert Law equation:

$$K = \frac{A - A_0}{C \times \frac{H}{L}} \quad (11-1)$$

where A is base-line absorbance, C is concentration, L is thickness of the disk area exposed to the beam, H is the band width at one-half the height of absorbance, and K is an absorption coefficient. In Table 11-5 are given the results of some analyses using these procedures. It is shown that the amount found agrees within 2% with the declared amount.

Susi and Rector⁴⁵ used a vibrator-grinding procedure to analyze mixtures of pesticides. A mixture of 1,1-bis (4-chlorophenyl) trichloroethanol and 1,1-bis (4-chlorophenyl) trichloroethylene, and individual pesticides were determined with an accuracy of 5%.

The rapid separation and identification of fractional milligram amounts of compounds may be effected by combining paper chromatography with infrared spectroscopy. An example of this combination is the separation and identification of cortisone and hydrocortisone in amounts 50 to 1460 mcg.¹⁹ The steroids were separated on Whatman No. 1 paper using a chloroform-formamide solvent system. The steroid zones were parti-

TABLE 11-5. RECOVERIES OF SOME PHARMACEUTICALS

Active Ingredient	Sample Description	Added, or Declared (per tablet, mg)	Infrared (mg)	Found (%)	Other Methods (mg)	Other Methods (%)
Hydrocortisone +	Tablets	20.0	9.5	47.5	*8.6	43.0
17-hydroxy-11-desoxycorticosterone			10.5	52.5	*11.2	56.0
Acetophenetidine +	Tablets	162.2	147.0	90.6	**146.5	90.3
Caffeine		32.4	29.5	91.0	**28.6	88.3
Ethisterone	Tablets	25.0	25.3	101.2	**24.7	98.8
Warfarin	Tablets	10.0	10.9	109.0	**11.4	114.0
Meprobamate	Crystals	10.5	10.3	98.1		
Phenobarbital +	Tablets	32.4	32.1	99.1	*31.6	97.5
Aminophylline						

- * Gravimetric
- ** Ultraviolet

tioned between chloroform and dilute hydrochloric acid. The chloroform extracts were evaporated to dryness under nitrogen. For amounts greater than 500 mcg, the above mentioned hand-grinding procedure was adequate. Modifications were required for amounts less than 500 mcg in which the residues were ground with 40 mg of potassium bromide and were pressed into 3 x 10 mm windows in pressed paper or potassium bromide peripheries 12.7 mm in diameter. Amounts less than 100 mcg required compensation with a corresponding blank and expansion of the absorbance. The blanks were prepared by extracting, from the same chromatogram, paper zones which compared in weight to the steroid zones. A potassium bromide plate was made of this blank in the same manner described above. By adjusting the blank plate in the reference beam to compensate for the impurities in the steroid plate, spectra of excellent quality were obtained. Estimations to within 90 to 105% of the applied steroids were reported. Because of the increasing use of paper chromatographic separations, it is anticipated that this general method will be applicable to a variety of compounds.

As another example, infrared spectroscopy was combined with paper chromatography for the identification of sulfanilamide which was a contaminant in a sulfacetamide powder.¹⁹ The two compounds were separated on filter paper impregnated with formamide. Chloroform-tertiary butyl alcohol (100:6) was the mobile solvent. Identification was achieved

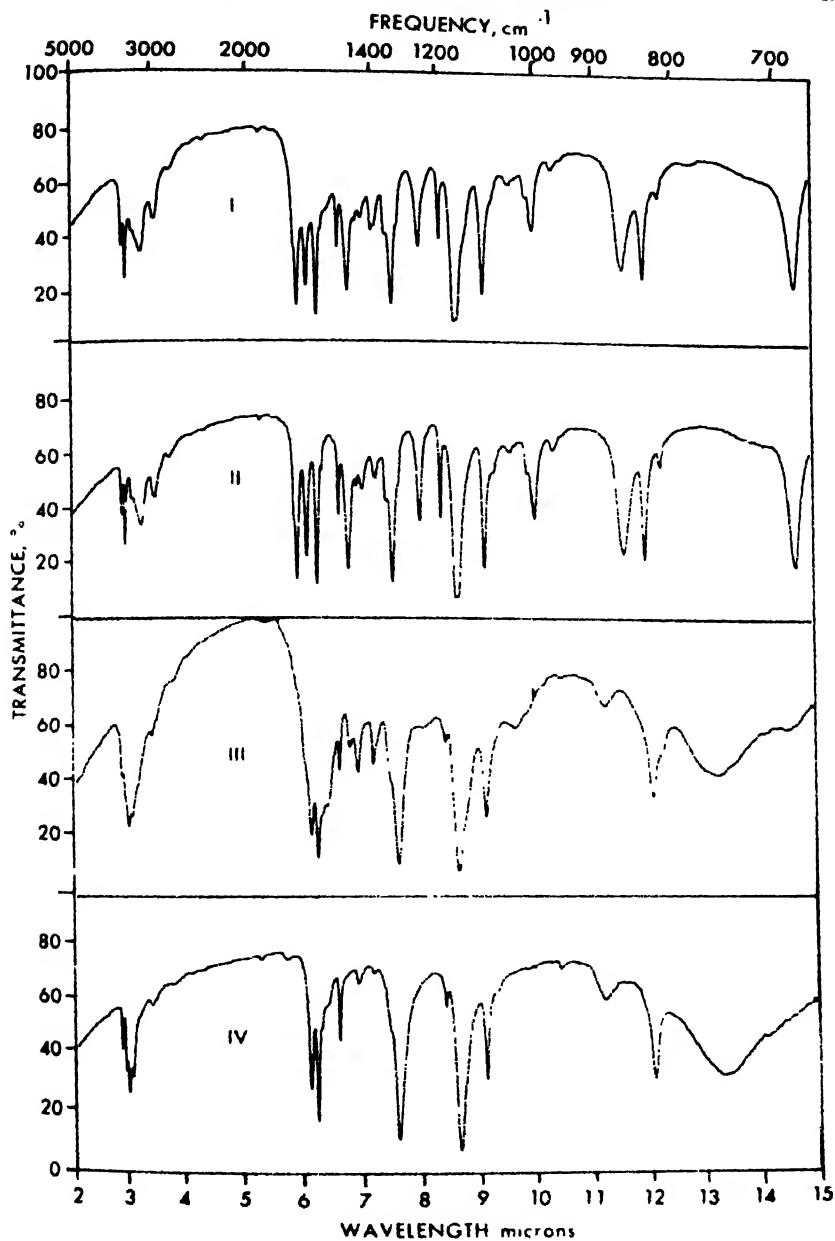


FIGURE 11-9. Infrared spectra of sulfacetamide (I) and sulfanilamide (III) isolated from paper chromatogram and the corresponding standard compounds (II) and (IV) as KBr disks and microplates (0.2 to 0.4%).

by comparison of the spectra of potassium bromide disks and plates of the extracted compounds (I and III) and the corresponding standards (II and IV) as shown in Figure 11-9. A determination of the amount of sulfanilamide in the sulfacetamide powder was made from quantitative spectra of the maxima at about 9.16μ .

Recently, infrared spectroscopy was used in the identification of compounds separated by thin-layer chromatography. In this work, a continuous extractor was employed to isolate the compounds from the chromatogram substrate,¹¹ Figure 11-10. In operation the thin-layer zone is placed in the column (B) which contains a pledget of glass wool. The zone may be pre-washed with a solvent. The apparatus is assembled and 2 ml of the extracting solvent are poured through the column and are collected in the boiling flask (A). The solvent is refluxed and the compound is extracted continuously from the thin-layer substrate by the condensate. The extract is evaporated to dryness and the residue is dispersed in a potassium halide micro-plate or is dissolved in a suitable solvent and the infrared spectrum is recorded.

By the use of micro windows (2×10 mm) in pressed paper or cardboard peripheries 13 mm in diameter,¹⁹ only 20 mg of the potassium halide is required for the spectrum of as little as 50 meg of an organic compound. The method is made more sensitive by localizing the compound in the central area of the 2 by 10 mm window with the potassium halide used to fill in the window area. In this way, the spectra of 10 meg of some compounds are obtained without the need for ordinate expansion or beam condensing.

In Figure 11-11 are shown the spectra of butabarbital isolated from a thin-layer chromatogram (I) and the corresponding standard compound

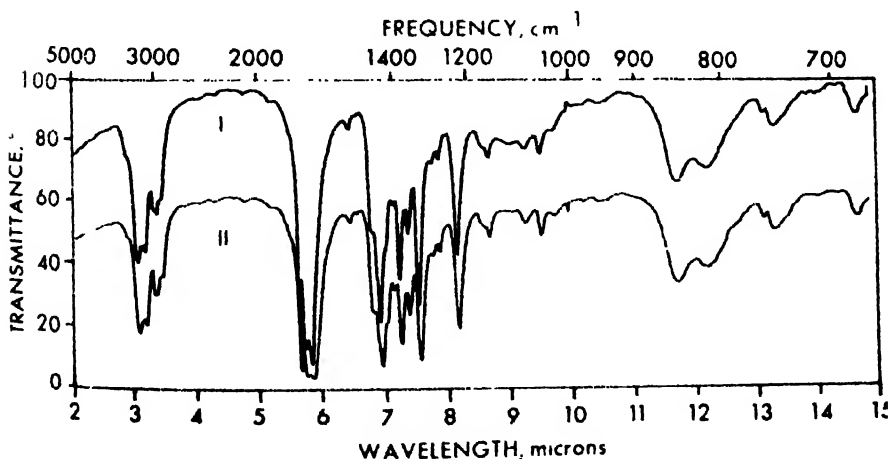


FIGURE 11-11. Infrared spectra of KBr plates (0.5%) of butabarbital isolated from thin layer chromatogram (I) and the standard compound (II).

(II). The spectra show no interference from the thin-layer substrate silicic acid, or the binder calcium sulfate.

Figure 11-12 shows the spectrum of testosterone (I) which was separated from a commercial mixture of steroids by thin-layer chromatography⁴⁸ and was isolated with the continuous extractor (Figure 11-10). Identification of the residue was made by comparison with the spectrum of standard testosterone (II).

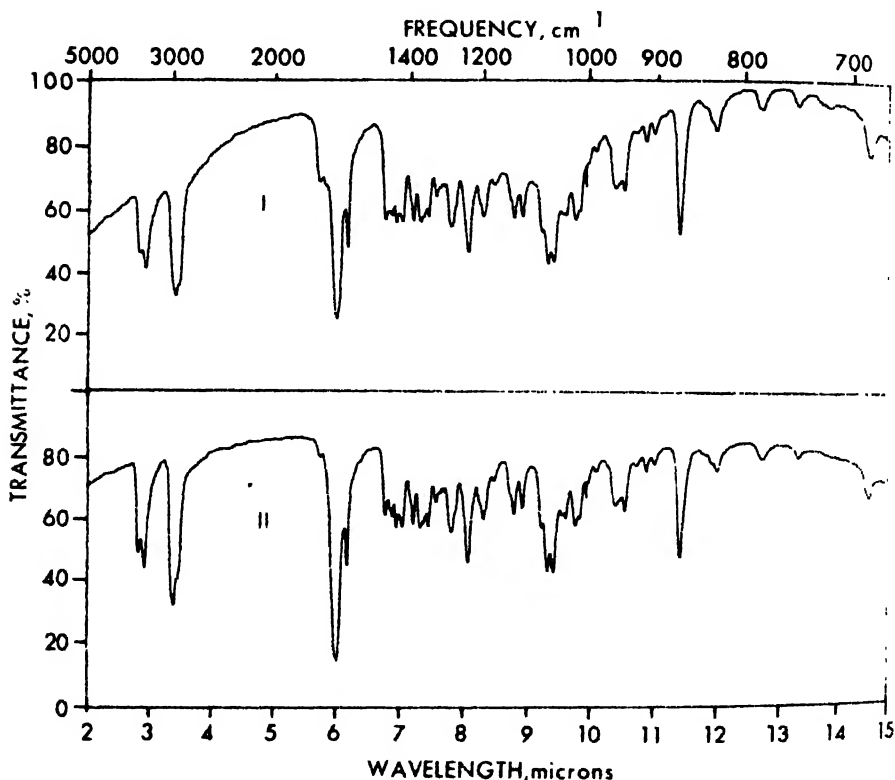


FIGURE 11-12. Infrared spectra of testosterone isolated from a mixture by thin layer chromatography (I) and the standard compound (II) as KBr micro-plates.

Gas chromatography offers an excellent means of separating pharmaceuticals from related compounds and contaminants. In an application of these methods to a commercial tablet of methyltestosterone, the steroid was condensed from the gas chromatograph stream onto 5 mg of potassium bromide powder.⁴⁸ The mixture was pressed into the central area of a 20

mg micro-plate. In Figure 11-13 are shown the spectra of the chromatographed methyl testosterone (I) and the reference standard (II).

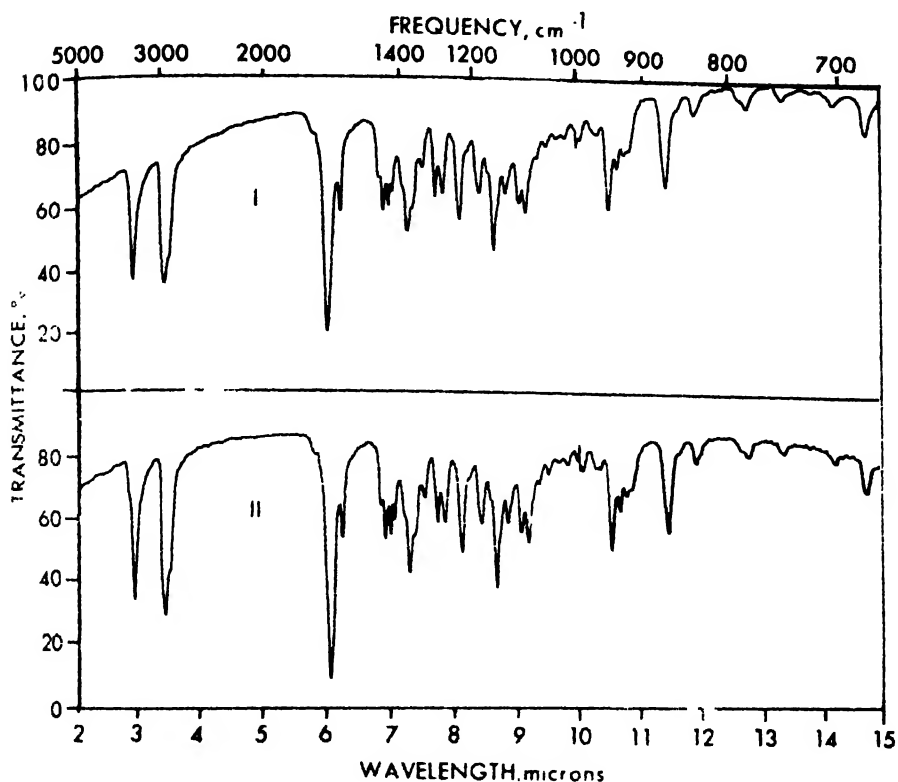


FIGURE 11-13. Infrared spectra of methyl testosterone isolated by gas chromatography (I) and the standard compound (II) as KBr micro-plates.

As the problems confronting these regulatory agencies become more complex, the need for research and development will become more pronounced. Research involving microquantities, differential spectrophotometry, and improvements in present analytical procedures will be required.

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CHAPTER

12

Infrared in the Industrial Laboratory

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INTRODUCTION

In the approximately twenty years since the introduction of commercial infrared spectrophotometers, infrared methods have become well established in the larger industrial laboratories and are rapidly becoming widely used even in the smaller laboratories. Some of the reasons for the acceptance of this technique are its unique potentialities combining speed, specificity, and applicability to a wide variety of analytical problems. Introduction of the low cost, mass-produced infrared spectrophotometers which are capable of efficient and quantitative performance under ordinary laboratory conditions, and of a wide variety of accessories, has accelerated this growth remarkably in recent years.

Increasingly, laboratories are finding it necessary to become involved in infrared spectroscopy because of the desirability of performing the analyses required to meet the buying specifications of their customers, or of examining a raw material or controlling a process for which purpose other analytical methods are either not available, or are inconvenient. In many cases, this has been done with some trepidation because of the degree of training required of the operators and supervisors, and because of the complexity of the theory. The practice of infrared spectroscopy, however, is not more difficult than that of ultraviolet spectroscopy, gas chromatography, colorimetry, or gravimetry, and it is usually found that after a short period of adjustment, applications will produce striking results which easily justify the investment in equipment and training.

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The experience in most analytical laboratories is that adoption of any proven technique will pay for itself in new information about products and processes. The problem then becomes: given a fixed amount of money, in what way can investment in new techniques be made to produce the greatest return? It is intended that the information given here will help in making a fair estimate of the capabilities of infrared spectroscopy and will thus aid in reaching an answer to this question.

APPLICATIONS

The two major applications of interest to the analytical chemist are qualitative and quantitative analysis. The many other applications of infrared spectroscopy such as determination of molecular structure, reaction kinetics, and the other physicochemical studies are not normally encountered in industrial analytical laboratories.

Quantitative Analysis

The fundamental basis of quantitative analysis by infrared spectroscopy is that molecules have characteristic absorption bands and that the amount of absorption can be related to the number of molecules in the absorbing layer. In the ideal case, this relationship is expressed by Beer's Law: $c = A \cdot ab$; where c is the concentration of the absorbing species, b is the thickness of the absorbing layer, a is the absorptivity of the pure species and A is the measured absorbance. Although this strictly linear relationship between absorbance (defined as the negative logarithm of the transmittance) and concentration is not always found, a reproducible nonlinear relationship is as useful and has been the basis of many practical methods (see Chapter 2).

One of the features of infrared absorption that makes it useful in analysis is that many structural groups of molecules are relatively little affected by the nature of the remaining parts of the molecule. This has made it possible to correlate infrared absorption with structure, and to perform structural group analyses. Examples of some of these are the determination of the amount and type of unsaturation in organic compounds.

Determination of Unsaturation. Methods for *trans* unsaturation in fatty acids and esters have been reported by Shreve, *et al.*³⁴ and others, and are included in "Official and Tentative Methods of the American Oil Chemists Society."²⁸ Methods for terminal unsaturation, in which it is possible to differentiate compounds with different degrees of olefin substitution have been reported by Anderson and Seyfried,³ and Saier, *et al.*³² In these methods, the weighed sample is dissolved in a suitable solvent, transferred to the infrared sample cell and the infrared spectrum determined. The

analytical results are calculated from the determined spectrum. Total analysis time is about 15 min, and the results are not obtainable as inexpensively or as easily by any other combination of methods.

Aliphatic Amides. The determination of aliphatic amides in the presence of several kinds of impurities is most difficult to make by any technique other than infrared spectroscopy. In the three methods reported by Miller²⁵ and Mallery,²³ the analysis is performed by dissolving the sample in chloroform and comparing the absorption of the amide carbonyl group to that of the pure material. When interfering constituents are present, preliminary separation by passage of the sample through a monobed ion exchange resin is usually sufficient to remove the ionic materials which account for a large proportion of the materials which can interfere with the amide determination.

Acetate Ester Content of Formate Esters. Infrared spectroscopy provides a rapid method for the determination of acetate ester content of many formate esters, such as geranyl formate, used in perfumes. The presence of acetate ester in these materials usually arises from the use of formic-acetic anhydride to prepare the formate. This analysis, which has been reported by Fenton,¹² can be performed because of the characteristic absorption bands of formate and acetate esters.

Determination of Hydrocarbon Content. A recent study of the long-wavelength tetramethylene band (720 cm^{-1}) illustrates that structural group absorptions are not necessarily limited to those showing chemical reactivity.³⁵ This absorption band is present in compounds which have an unbranched carbon chain at least four carbons long, and has been shown to be quantitatively related to the "hydrocarbon" content of the material.

Methods Based on Functional Group Absorption. From the above examples, it can be seen that a fruitful area of application is that of analyses based on the presence of a structural group in the desired constituent. In general, any molecular structural feature which remains little affected by the adjacent molecular structure can be expected to have a characteristic infrared absorption band which may be usable for quantitative analysis. Some examples of methods based on these characteristic infrared absorption bands are listed in Table 12-1.

Methods Specific for Single Compounds. An even wider variety of materials can be determined by measurement of an absorption specific to a single compound which serves to differentiate it from other components of the sample. For example, analysis of mixtures of up to 16 various chlorinated phenoxyacetic acids has been reported using component specific bands in the fingerprint region (7 to 15μ).¹⁹ In another method, eleven polymethyl benzenes are determined in mixtures by measurement of the absorption between 11 and 15μ .¹⁶

TABLE 12-1. PARTIAL LIST OF INFRARED METHODS
BASED ON FUNCTIONAL GROUP ABSORPTION

Group	Wavelength (μ)	Reference
OH	2.99	3
nonaromatic CH	3.4	15
CHO	3.63	3, 31
COOH	3.82	3
C \equiv N	4.48	1
CO	5.8	3
CONH	5.96	23, 25
CH ₃ COO	9.6	12
Unsaturation	10 to 12	3, 28, 32, 34
CCl	13.4	36

Since every nonlinear chemical compound has $3N-6$ (where N is the number of atoms present) vibrational frequencies to start from, the probability of finding an absorption band characteristic of the compound which can be measured in a mixture is reasonably high. A series of methods which are, in general, of this type have been published in "Analytical Chemistry" under the heading *Infrared Quantitative Analysis Data* and are currently appearing in *Applied Spectroscopy*. These methods, collected with the aid of the Coblenz Society, illustrate the range, simplicity and accuracy of infrared spectrophotometric methods. An index to the first 178 of these methods has recently been published.⁴

Nonspecific Methods. In addition to the methods specific for a single compound, a large group of methods has been devised which measure an absorption characteristic of a class of chemical compounds. Examples of these are the functional group procedures, such as hydroxyl value and carbonyl value, in which chemical attributes of the sample can be determined almost irrespective of the identity of the component or components possessing the functional group.^{2,13} This approach may be used in the various tracer methods. An example might be the determination of the flavor content of a product by comparing the extractable aldehyde content with that of the flavoring mixture used.

Another class of nonspecific methods is that in which deviation from a standard is measured without specifying the cause of the deviation. For example, one might obtain the infrared spectrum of a mixture at two acceptable extremes of its composition, and use as a specification that acceptable product must lie between the extremes.

Value of Infrared Specificity. The major characteristic of infrared spectroscopy which makes it so useful in quantitative analysis is its specificity. This feature frequently permits one to perform the analysis with no, or very little, pretreatment of the sample. Constituents which are likely to

interfere in wet chemical procedures can be of little concern in the infrared methods. This specificity also permits performing analyses which can be exceedingly difficult by other methods. Infrared procedures are used to determine relative amounts of conformational isomers, positional isomers, and other combinations of materials so close in their chemical and physical behavior that infrared spectroscopy was the means by which the differences were first detected.

Infrared spectroscopy has also been of considerable use in the analysis of polymers (see Chapter 8), and methods have been reported for ethylene-propylene copolymers,¹⁰ rubber mixtures,⁷ acrylonitrile-styrene copolymers,³¹ polysiloxanes¹⁴ and many others.

Inorganic Applications. While the examples cited above have referred to organic materials, infrared methods are equally applicable to many inorganic systems. For example, methods have been reported for the condensed sodium phosphates⁸ and the hydrates of calcium sulfate.²⁶ General considerations in inorganic analysis have been discussed with descriptions of methods for quartz in industrial dusts, CO₂ content of phosphate rocks, and lithium-aluminum ratios in lepidolite micas¹⁸ (see Chapter 17 on Inorganics).

Qualitative Analysis

The specificity which guarantees the usefulness of infrared spectroscopy for quantitative analysis is responsible for its power as a qualitative technique. This power is great enough to insure that it be the technique of choice for qualitative analytical problems. Enumeration of the cases in which infrared alone has provided the desired identification of an unknown material would fill several books. In most laboratories, more time is spent on qualitative than quantitative analysis. This use, occupying the most time and expense, has also been the object of the greatest attention, and the opportunity for the development of the greatest number of techniques and the accumulation of the most data.

While the theoretical interpretation of infrared spectra has received much attention, the greatest practical value has been realized by the empirical and semi-theoretical correlation studies. Empirical correlations have been the subject of a number of excellent books and book chapters and an impressive list of journal articles. While the interpretation of infrared spectra is gradually becoming more scientific, it is still, in practice, more correctly described as an art.

Value of Preliminary Separation Procedures. As the complexity of unknowns increases, the possibility of making successful identifications of the components by direct infrared examination decreases, and the many separation procedures become increasingly important adjuncts to the infrared technique. When frequent samples of a certain type are received for

analysis, such as plastics, flavoring materials, or consumer products, it is possible to develop a sample separation and examination scheme that will identify the constituents to almost any degree of completeness. These schemes can be based on solvent extraction, adsorption chromatography, ion exchange, and gas-liquid partition chromatography steps for the separation of the material followed by infrared analysis of the separated fractions. Similar analytical schemes can be used for the identification of impurities and minor ingredients, the characterization of competitive products, and the determination of the nature of sludges, slimes, or by-products.

Application of infrared spectroscopy to the qualitative identification of relatively pure materials has been the subject of innumerable articles in the literature. It is unfortunate that more has not appeared describing techniques applied to the slimes and gums frequently received for identification, and on the well-developed procedures used for the examination of industrial or consumer products. The paucity of published information is in great part due to the competitive advantages which accrue to the possessor of such procedures, and to the general lack of interest noncommercial groups have in commercial products.

Many collections of spectra devoted to a single class of materials have appeared in the literature. Among them are plastics and resins,^{19,21} pesticides,⁶ steroids,⁹ plasticizers,¹¹ and inorganic compounds.^{22,24} Collections like these are valuable and can provide the framework around which a separation scheme can be developed.

Evaluation of Other Analytical Methods. Another application of infrared spectroscopy is in the evaluation of other analytical procedures. In the separation of a complex mixture by chromatography, identification of the eluted fraction may determine the applicability of the chromatographic procedure. If an unexpected precipitate forms in a chemical procedure, infrared examination frequently can pinpoint the material causing the difficulty. Extensive use of infrared spectroscopy has been made in identifying components eluted in gas-liquid partition chromatography. By careful handling, infrared spectra can easily be obtained on 50 to 100 μ g of sample, and with extensive precautions, this range can be reduced another order of magnitude.

Limitations of Infrared. Despite the wide applicability of infrared spectroscopy, there are many cases where it should be considered only as a last resort. Such areas of difficulty include determination of subjective properties of materials, direct comparison with shorter chemical methods, and analysis of aqueous solutions.

Subjective properties of materials, such as odor, taste, feel, etc., are almost always a complex function of the composition, and are best measured

directly by test panels. When infrared absorption can be related to these properties, one must be prepared to encounter the exceptions and to accept a high variance in the analytical result.

Also, one should not expect infrared methods to take over for the shorter chemical methods. Many analytical problems can be solved more quickly and cheaply by a rapid spot test, or simple titration, and these analyses should be performed in the most economical way. One should be careful about infrared methods which are only moderately shorter than accepted wet chemical methods and are expected to give essentially the same result. In many cases, the results by the two methods fail to agree, and the work required to establish the applicability of the infrared method and to explain the difference in the results may cost more in time and effort than can be saved by the shorter method.

Aqueous Solutions. Until recently, infrared work with aqueous solutions was quite difficult. Because of the strong absorption of water and the relative lack of water insoluble optical materials for the construction of cells, analysis of aqueous systems was avoided by the infrared analyst. The recent introduction of infrared transparent glasses may go a long way toward changing this situation.²¹ The strong absorption of liquid water is not so easily avoided, however, and analysis is still limited to the use of concentrated solutions and the use of narrow regions of the spectrum. The use of deuterium oxide as an aqueous solvent has permitted some extension of the spectral region. However, a new set of difficulties can be introduced—such as hydrogen-deuterium exchange and a resulting alteration of the absorption spectrum.²⁰

The Economic Gains from Use of Infrared. It is difficult to evaluate the economic advantage of using infrared spectroscopy. The greatest financial rewards derive from the increase in knowledge one obtains about processes and materials, and this is not usually amenable to economic analysis. It is not easy to set a monetary value on the knowledge that 10% of a pilot plant stream is by-product A rather than by-product B.

Of more direct accessibility, however, is the high capacity and rapid analysis afforded by the technique. As an average, an infrared method requires about 10 min of instrument time and very little more in analyst time. Sample preparation steps do not usually diminish the instrument capacity.

TECHNIQUES

Quantitative

Gases. In the ideal infrared method, the sample is introduced directly into a suitable sample cell and the infrared spectrum measured. Most

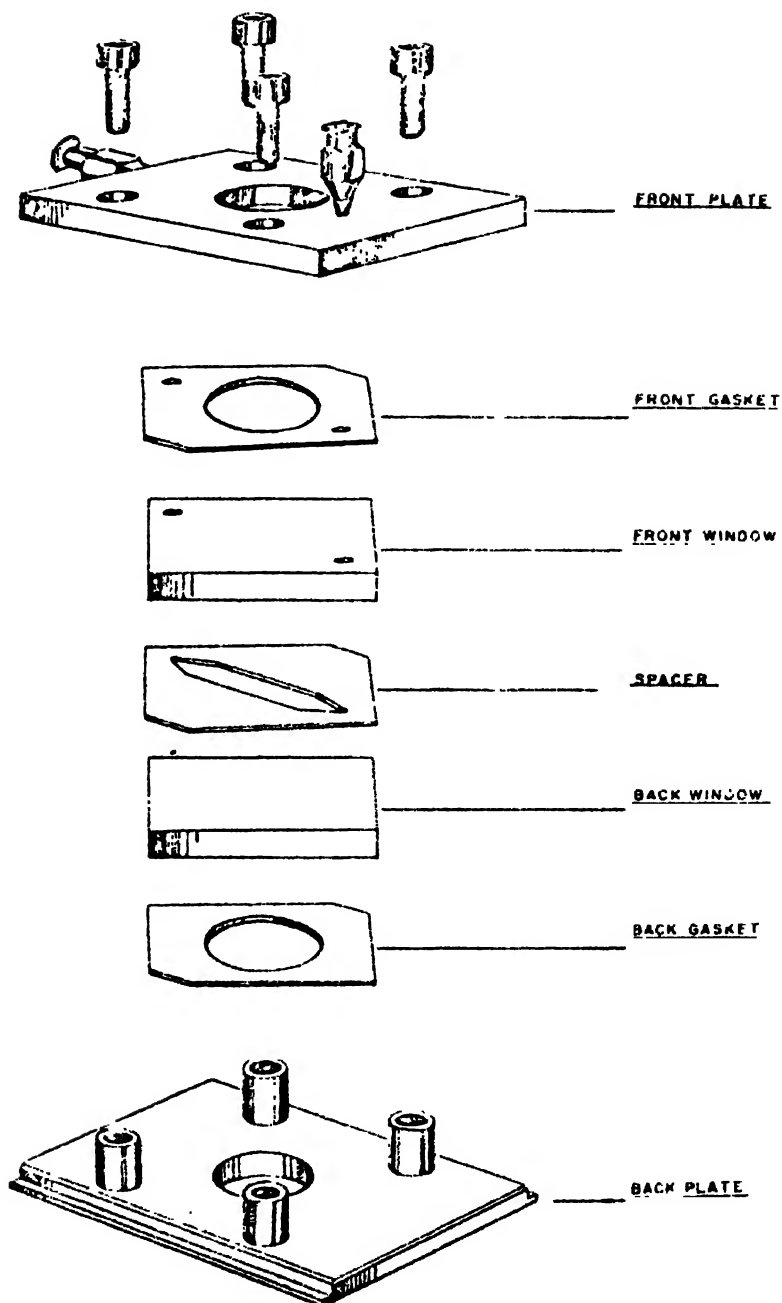


FIGURE 12-1. Fixed thickness sample cell.

analyses of gaseous samples can be performed in this way. Using a suitable gas handling system, the sample is introduced into a standard long path length gas cell for measurement. Since temperature and pressure conditions of the gas affect the amount of sample in the light path, careful control over these variables must be maintained in order to obtain the maximum accuracy.

Liquids and Solutions. Many liquid samples can be introduced directly by means of a hypodermic syringe into a standard fixed thickness cell of the type shown in Figure 12-1. Solid samples can frequently be dissolved in suitable solvents and similarly introduced into liquid sample cells. Since most solvents have absorption spectra of their own, choice of a solvent which will dissolve a suitable concentration of sample and yet not interfere with the absorption bands of the sample which it is desired to measure can become a problem. A wide variety of solvents has been used. Most of the laboratory supply houses offer charts showing the more common solvents and the spectral regions in which they are useful.

Solids.

Mulls and internal standards. Solid sample which cannot be obtained in solution form may be examined as dispersions in liquids or as dispersions in solids. In the first case, the sample is finely ground in a mortar with the dispersing liquid, such as mineral oil or, more desirably, dodecane nitrile, until a thick paste is prepared. The paste, or mull, is spread between the windows of a demountable sample cell (Figure 12-2) and the infrared spectrum determined. Variations in thickness are obtained by using spacers of lead or aluminum foil, or by use of a special demountable cell with a tapered sampling space. With a double beam infrared spectrophotometer, it is possible to subtract the spectrum of the mulling agent by placing a compensating amount of mulling agent in a second demountable cell placed in the reference beam of the instrument. The advantage of using dodecane nitrile for this purpose then becomes apparent, since one can adjust the amount in the reference beam to just compensate for the nitrile band at 4.5μ .

Such sample preparations are difficult to measure quantitatively since the mull can neither be prepared nor transferred quantitatively to a fixed area of the sample cell. To avoid this difficulty, it is possible to use an internal standard approach. An internal standard is chosen with an infrared absorption band in a free region of the sample spectrum. A known mixture of the internal standard and the sample are weighed together and mulled as before. By comparing the ratio of absorbance of the sample to that of the internal standard, a measure of concentration is obtained. Inorganic materials are

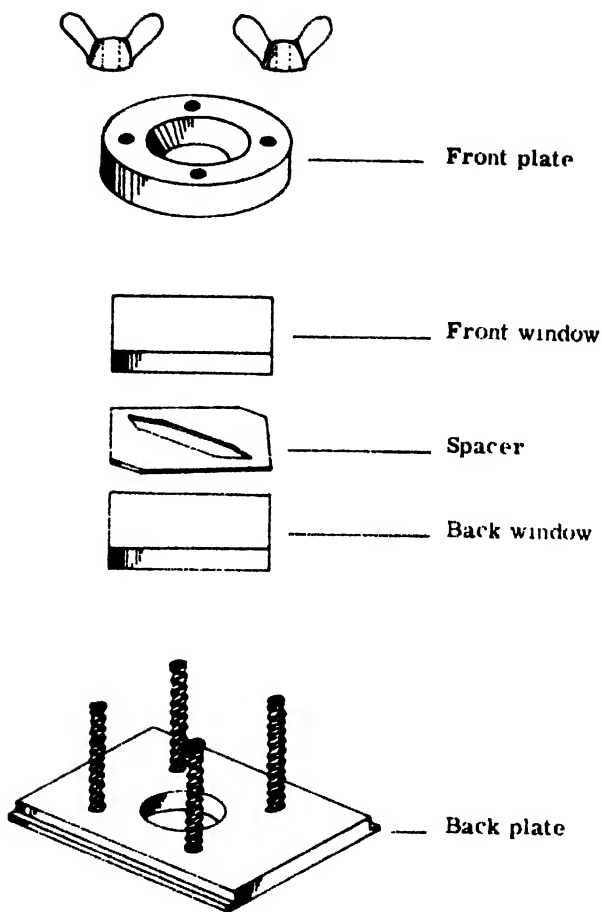


FIGURE 12-2. Demountable cell.

frequently used as internal standards because of their generally simpler spectra, sharper bands, and ease of grinding and mulling. Some materials that have been used are PbCNS , CaCO_3 , dodecanitrile, anthracene, and metal stearates.

The pressed disk. An alternate way of handling solid samples is the use of the pressed halide disk. Most commonly, the sample is mixed in weighed proportion with KBr , finely ground, and pressed in a die at pressures of about 30,000 psi until the disk becomes transparent. By careful attention to weighing and grinding, and with the use of a properly designed die, quantitative results can be obtained.

One difficulty in handling solid samples is caused by the occurrence of polymorphic forms of the sample constituents. Usually the spectrum of a solid organic material is markedly dependent on the crystalline phase present. In handling solids, care must be taken to preserve the proper polymorphic phase of the sample. On occasion, thermal tempering steps may be required to obtain the sample in reproducible form.

The Differential Technique. Once the sample can be obtained in a suitable form for measurement, the choice of measurement techniques must be made. It is usually adequate to measure the peak height above base-line and relate this to concentration.

The use of a differential technique, in which a carefully chosen blank is placed in the reference beam of the double beam instrument, and its spectrum subtracted from that of the sample, offers advantages where higher accuracy or greater sensitivity is desired. In this approach, the blank components are added to the reference cell in such concentrations that they balance the amount present in the sample. The determined spectrum, then, is that of the desired constituents only, free of the interference of the blank constituent. When a fixed amount of the component to be determined in the sample is added to the blank cell and the resulting difference spectrum expanded by increasing the cell thickness or by using instrumental scale expansion, increased accuracy can be obtained.

Occasionally, the differential approach may be doubled up for the determination of low concentrations of material. In this "double differential" method, the spectrum of the sample versus a suitable blank is determined, then the sample and blank are exchanged in their cells and the spectrum redetermined on the same chart. By measuring the total of positive and negative peaks, now double in height, increased sensitivity may be obtained. By use of this technique, ppm quantities of material may be determined in favorable cases.

An excellent description of these general techniques used in quantitative analysis has been prepared by Committee E-13 of the American Society for Testing and Materials entitled, "Recommended Practices for General Techniques of Infrared Quantitative Analysis."³⁰

QUALITATIVE ANALYSIS AND THE REFERENCE SPECTRA FILE

The most important tool used in the identification of an unknown is the memory of the interpreter. The more experience he has, the more likely he is to come to a rapid and correct conclusion regarding the nature of the unknown. A positive identification can be considered made when the unknown spectrum can be matched point by point with that of a known compound.

An empirical basis of interpretation has been established by the many studies of the correlations observed between organic structure and spectra. Extensive compilations of these correlations have been published, and journal articles reporting new studies and refinements of the old appear every month. Usually the interpreter uses studies of this sort to suggest a number of structural features likely to be present in the unknown. Having gone as far as he can from these sources of information, he then turns to a file of reference spectra, making directed searches until a satisfactory match is obtained.

For a pure compound, the spectrum of which is already in the reference file, the identification is usually straightforward. As the nature of the unknown deviates from that of the compounds in the file, and as the number of components in the unknown increases, identification becomes more and more difficult, and more of an art than a science.

In this last stage of interpretation, much depends on the content of the reference file and on the accessibility of pertinent spectra. The larger the reference file, the more likely that an identification is possible, but also, the more difficulty one has in entering it and finding suitable spectra. Many laboratories have found that the best way to obtain a large reference library is through the purchase of one or more of the commercially available sets. More than 55,000 reference spectra are available in this manner and more are being added each year. Sources of these spectra are listed in Table 12-1.

TABLE 12-2. CATALOGS OF INFRARED SPECTRAL DATA *

- Standard and Commercial Spectra; The Sadtler Research Laboratories 3314-20 Spring Garden Street, Philadelphia, Pennsylvania
Documentation for Molecular Spectroscopy; Butterworth Scientific Publication, London, WC2.
Infrared Spectral Data; American Petroleum Institute, Research Project 44, Chemistry Department, Agricultural and Mechanical College of Texas, College Station, Texas.
Infrared Spectral Absorption Data, National Research Council-National Bureau of Standards, Washington 25, D.C.
Coblentz Society Collection; Distributed by The Sadtler Research Laboratories, 3314-20 Spring Garden Street, Philadelphia, Pennsylvania.
Manufacturing Chemists Association Research Project, Chemistry Department, Agricultural and Mechanical College of Texas, College Station, Texas.
Infrared Data Committee of Japan, Sanyo Shuppan Boeki Co., Inc., Hoyu Bldg., 8-2-chome Takara-cho, Chuo-Ku, Tokyo, Japan.

*Serial number and molecular formula lists of these spectra can be obtained through the American Society for Testing and Materials, 1916 Race Street, Philadelphia 3, Pennsylvania.

Indexing Systems for the Reference Spectra File

The utility of the reference spectra file is directly dependent on the utility of the indexing system. With small files, indexes can be made alphabetical

or by chemical classes, and, with sufficient cross indexing, such a manual index can accommodate several thousand spectra. As the file increases, however, the manual index becomes less and less satisfactory and recourse must be made to a mechanical system of handling searches.

The American Society for Testing and Materials (ASTM) prepares and distributes three mechanical index systems for searching and correlating infrared spectra. The data for these systems are abstracted by ASTM Committee E-13 from all of the spectra collections listed in Table 12-2 and from spectra published in the literature.

Wyandotte-ASTM Punched Card Index. The first system, the Wyandotte-ASTM Punched Card Index for Spectral Absorption Data, was developed at Wyandotte Chemicals Corp. by Dr. L. E. Kuentzel. The index consists of standard IBM cards punch-coded with structural information, elemental composition, and position of the prominent infrared absorption bands for each of the compounds for which infrared spectra are available. With this index and a card sorter, rapid and efficient searches can be made for specific compounds, specific functional groups, or compounds exhibiting absorption bands at specific wavelengths.

Magnetic Tape and Digital Computer. The second system comprises the same data stored on magnetic tape, and a computer program, also on tape, to provide sorting facility. The magnetic tape system provides several advantages but requires the availability of a digital computer. The sorting programs are generally useful for retrieving any kind of data which can be stored in punched card format.

Optical Coincidence Index. The third system is the ASTM Infrared Optical Coincidence Index. This set currently contains the data for 9251 spectra coded on optical coincidence or "peek-a-boo" cards. In this system, a single card represents a single characteristic of a compound (such as an infrared band at 5.8μ or the presence of sulfur), rather than the compound itself. Numbered holes drilled into a rectangular grid represent the serial numbers of the compounds included in the index. By superimposing the cards representing the characteristics of an unknown, the points at which light shines through all the cards represents the reference compounds which have the same characteristics as the unknown. Descriptive booklets describing these systems are available from ASTM.⁵

Commercial Suppliers' Indexes. In addition to these systems, commercial suppliers of infrared reference spectra have usually provided some means of indexing their own spectra. For example, the DMS spectra can be purchased on edge punched cards for manual sorting, and an optical coincidence system is now available. The Sadtler collection is indexed by a "Spec-finder" which is essentially a dictionary listing of the spectra in order of their strongest infrared bands.

More advanced systems are currently under study, but no highly promising approach has yet been discovered. Most particularly, none of these systems is satisfactory for mixtures, thus they require some judicious decisions to allow for impurities.

SETTING UP AN INDUSTRIAL INFRARED LABORATORY

In setting up an infrared analytical laboratory, several questions are presented: what type of personnel are required for operation and supervision, what is needed in the way of space and services, and what auxiliary equipment must be provided?

Personnel

Many successful installations have been made in which the laboratory personnel are trained on the job in the operation and maintenance of the equipment, the supervision not having previous experience in the technique. No special training over that of ultraviolet spectroscopy is required of the operators which cannot be picked up by reference to this or any other of the several books and articles in the literature. Any additional training which can be provided, however, will be quite rewarding. The equipment operators may be chosen from the group normally able to handle analytical work with accuracy and some degree of judgement. An interest in electronics and mechanics is desirable, as is a bent toward gadgeteering. While complex servicing may best be handled by the service engineers of the instrument manufacturer, day to day maintenance and the more routine service jobs can be readily performed by the operators.

Ideally, the supervisor should be chosen for his interest in mastering the new technique, general ability at analytical thinking, and perhaps a greater orientation toward research than production. While at first the factory infrared work will be directed toward carefully formalized methods and techniques, there is considerable value to be obtained by extending the technique to the less formalized and more experimental uses. If the supervision is intrigued with the technique, this greater use will be more easily obtained.

In providing for effective supervision, some consideration should be given to providing a formal training opportunity, such as a tour of duty at an infrared installation already in the company, perhaps in the central research laboratory. In many ways, this is the most effective training that a supervisor can have, particularly if the program is set up to provide direct experience in those techniques expected to be of major interest in the factory laboratory. Frequently, however, a central research facility will be established on a different basis and on a much different scale than is expected of

the factory laboratory, and this must be taken into account in the training plan.

When a suitable laboratory is not available, consideration should be given to attendance at one of the several summer courses given at the various universities in the techniques of infrared spectroscopy. These courses usually run from one to two weeks and provide a suitable grounding in theory and the opportunity to obtain experience in laboratory operations. The oldest and best known is the course given at MIT. In recent years, however, courses have been instituted in several other places. A listing of these courses is usually given in the "Analyst's Calendar" section of *Analytical Chemistry*.

In one successful laboratory providing service for a development department, the infrared group is composed of two analysts and a supervisor. The analysts are high school graduates trained on the job in the standardized methods and techniques developed for this laboratory's use. The supervisor is a staff chemist whose background includes attendance at one of the college summer courses as well as several months' experience in the research laboratory infrared group. The supervisor performs most of the qualitative identification work which, with the overseeing of the analysts, requires nearly full time. He is also responsible for training an analyst to perform the more routine identification work. The sample load averages about 100 wk of which 75% are for qualitative identification. New procedures are provided by the research group; however, short quantitative procedures are devised on the spot for some samples.

Laboratory Facilities

The space required for an installation is about that used for any other analytical technique involving some sample preparation and the use of volatile solvents. A typical installation of 20 to 30 ft of bench space and a hood would accommodate an infrared instrument and auxiliary equipment. Since carbon disulfide is a frequently used infrared solvent, care should be taken to confine its handling to the hood and to prevent its contact with elevated temperatures. Because of its flammability, it is a hazard well below its auto-ignition temperature of about 125°C.

While the newer infrared instruments are less subject to damage by high humidity, it is highly desirable to have air-conditioning to provide a maximum of 50% relative humidity. Fogging of sample cells and spare optical components is much reduced and operations are simplified. If only normal laboratory air-conditioning is available, use of desiccators for storage of cells and components becomes more essential, and on occasions of high humidity, it may become necessary to curtail operations to reduce damage to cells.

Infrared Equipment

In addition to the infrared spectrophotometer, an assortment of spare parts, cells, and KBr disk equipment is needed.

Spare parts include the normal complement recommended by the instrument manufacturer, and a selection of electronic tubes, which are almost invariably the parts most subject to replacement.

A selection of fixed thickness cells, in matched pairs, will be required for quantitative work. A suitable range of sizes would include 0.01, 0.025, 0.5, and 1 mm thicknesses. A variable space cell is useful on occasion for balancing out solvent and blank constituents. Purchase of this item, however, can be delayed until more familiarity with instrument procedures is obtained. Demountable cells can be purchased or made in a local machine shop, according to the design in Figure 12-2. Usually three to six are required. Windows for the demountable cells can be purchased from any one of several suppliers.

The equipment for making KBr disks is valuable, but unfortunately is a relatively expensive part of the infrared laboratory. Items required are a high pressure press, a punch and die set, and suitable grinding equipment. The press should be capable of pressures of 20 tons on a 1-in. diameter die. The punch and die can be purchased from several sources or manufactured according to the plan in Figure 12-3. The most versatile grinders are the oscillating, or vibratory type in which the sample is placed in a capsule with a pestle or ball bearing and vibrated at high speed. It is convenient to have both the small and large size capsules available to handle both milligram and gram quantities of materials.

A desiccating cabinet is a useful adjunct for the storage of cells and spare cell windows.

Administration

Many administrative problems can arise over the source of the analytical procedures and the nature of the analytical demand. While these are not greatly different in kind from those that arise in other areas of laboratory operation, their difference in degree assures that a consideration of these problems will not be wasted.

Once a few successful applications have been made, there is usually no further difficulty in obtaining analytical problems for solution. At first, however, one may anticipate some reluctance to accept infrared data if it happens to conflict with a previously formulated hypothesis based on less accurate information. In this case it is wise to expend sufficient effort to provide adequate explanations of the techniques and data to overcome any resistance. Once this possible hurdle is passed, no problems in demand are

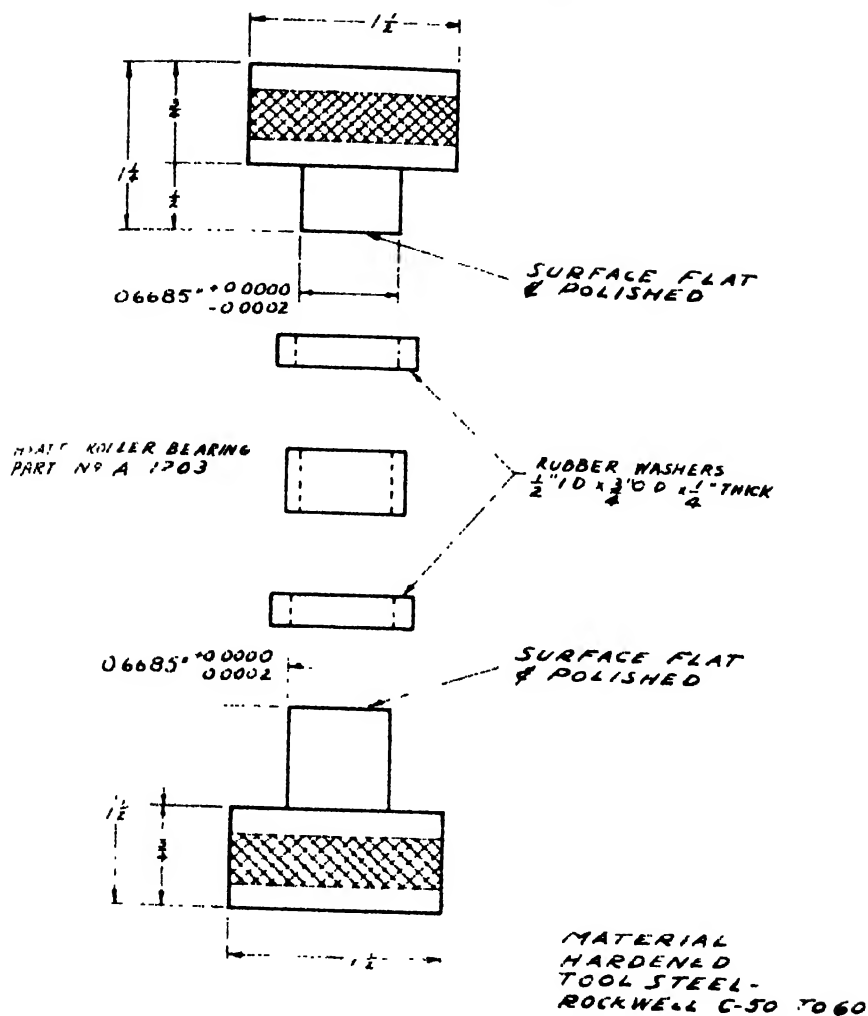


FIGURE 12-3. Die for pressing KBr discs.

likely to be encountered except that more analytical work is demanded than can easily be given.

Some laboratories have found it desirable to supply a formal training lecture on analytical facilities to new factory supervisors. The availability of such a training opportunity can solve a few problems in advance. The best time for education, however, is when there are specific problems in the laboratory. No opportunity should be lost at this time to be sure that the basis for the analytical results are thoroughly understood.

Method Development and Modification. In the favorable case, analytical methods will be initiated by a central research group. To these can be added many others reported in the literature, if sufficient time is granted for the ever-necessary modifications. Even when an adequate source of finished methods is available, it is necessary to allow a fixed percentage of time to the functions of development and method modification. Because of the specificity of the infrared method, there will be a considerable need and desire to apply the methods to samples which differ slightly from those encountered in the development of the method. The need for additional development time then becomes more pressing and less disruption of operations will occur if this demand has been anticipated. It is best to assign a specified percentage of time to this and the other necessary functions to be discussed below, in order to prevent production considerations from making inroads into this time.

Maintenance of Analytical Accuracy. The maintenance of analytical accuracy is a bigger problem with infrared analytical procedures than with most wet chemical methods. At the current state of the art, it is not always possible to transfer data quantitatively from one installation to another, or even to be assured that accuracy of calibration will be maintained with a given analytical setup over an extended period of time. This requires that each analytical procedure must be calibrated on each instrument, and that provision be made for instrument checks and occasional recalibration.

The most economical way to verify instrument calibration is to obtain appropriate standard samples which are periodically reanalyzed along with the current production samples. Most particularly, calibration should be re-checked after any maintenance has been performed on the equipment. This function can frequently be combined with the laboratory accuracy checking program and the results used for statistical determination of the accuracy of the methods, as well.

The most frequent cause of apparent change in calibration is the change in the thickness of the sample cells caused by erosion or dissolution of the cell faces, or the deposition of insoluble materials. A regular weekly schedule established for checking cells will avoid many uncertainties in the analytical results.

Reference Standards. Many problems will be encountered in obtaining and maintaining suitable reference standards for determining and checking calibration. Whenever possible, the calibration standard should be composed of pure synthetic chemicals of known structure, and should be stored in such a way that no change in composition is likely to occur. Since such samples may be quite expensive, or unavailable in sufficient quantity, larger amounts of a suitable secondary standard may be prepared for routine use. The secondary standard should be as pure and as stable as

possible, and should be carefully compared to the primary standard. Frequently, the secondary standard can be subdivided into amounts just sufficient for the recalibration procedure and stored in sealed ampoules under refrigeration. The accuracy of the analytical method can be no greater than the purity of the standard sample; therefore suitable provision for maintaining standards is essential.

In the absence of a primary standard, an arbitrary standard may be assumed. The composition of the material should be determined as accurately as possible, based on chemical analysis, or just on the fact that it is the purest sample that has been analyzed by the infrared method. In such cases, provision must be made for progressive changes in the standard as purer materials become available. Provision must also be made for the natural reluctance to accept changes in the basis of the analytical result. Appropriate designation of the meaning of the analytical result is, in this case, essential.

On occasion, it may be necessary to accept calibration data from the literature or from another installation. When this is done, attention must be paid to the conditions under which the data are derived and these conditions duplicated as nearly as possible. The magnitude of the errors involved have been measured, and under ideal conditions can be quite small. A comparison of data taken from A.P.I. spectra and a laboratory analysis has been reported³⁹ in which the standard deviation of the differences between results varied from 0.15% to 0.6% at the 35% level for mixtures of C₄ hydrocarbons.

Variations among Instruments. Not many studies of the magnitude of variation among different instruments have been reported. Results on the cooperative testing of the infrared *trans* method by the American Oil Chemists' Society indicate that for this method, the absorbance of a primary standard elaidic acid sample exhibits a coefficient of variation of 3% and a range of 11.5% over the 10 instruments used in 9 different laboratories.¹⁷ A later study of the secondary standards indicated a 95% confidence interval of about $\pm 3\%$ of the amount present,¹⁸ for this analysis.

In a comparison of Beckman instruments, reproducibility among new instruments was found to be very good using a rotating disk as a standard of transmittance.³⁷ In our laboratories, a study of ten Perkin-Elmer Model 237-B infrared spectrophotometers was made using tetrachloroethylene in a single fixed thickness cell. The coefficient of variation was found to be 2.7%. On an absorption band having an average absorbance of .354, the ten instruments ranged from .338 to .368.

Maintenance of Spectra File. In addition to the time required to maintain quantitative standards, provision must also be made for the maintenance of the laboratory file of reference qualitative spectra. After some time of

operation, the laboratory doing qualitative work will have accumulated a file of infrared spectra of materials most closely related to their own samples. This laboratory file will be used frequently and will be of considerable value. The time required to keep this file indexed and in good order should be considered part of the necessary analytical operation and charged accordingly.

Time Allotted to Supporting Functions. The amount of time spent on these supporting functions will vary widely with the nature of the laboratory operation. In many laboratories, the accuracy control operations do not greatly exceed that required for the wet chemical operations, and require from 2 to 5% of the operating time. In laboratories devoted largely to qualitative work, 10 to 15% of operating time may be devoted to the operations of maintaining the reference file and extending correlation studies. This time is usually returned directly in more rapid and complete qualitative analysis and is chargeable to the research and development function of the laboratory.

SUMMARY

In its approximately twenty years of commercial development, infrared spectroscopy has changed from a research laboratory curiosity to an almost indispensable part of the industrial laboratory. The characteristics responsible for this change are the specificity and speed of infrared methods. The development of simple techniques, and of relatively low cost equipment which is easy to operate and maintain, now places infrared spectroscopy within the ranks of the "easy" analytical techniques, assuring that it is not greatly different in operating simplicity from the wet chemical techniques commonly available.

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Infrared Plant Stream Analyzers

*A. M. Bartz and H. D. Ruhl**

INTRODUCTION

Infrared analyzers are among the most useful "on-stream" analytical instruments available to industry today. The advent of other methods of analysis serves to complement and broaden the use of instruments, and has, in the long run, resulted in an increasing demand for infrared analyzers. They are capable of operating under adverse conditions with excellent reliability. They can sample a stream continuously, analyze for a single component in that stream, and read out the concentration of that component in less than a minute. Potentially, instruments could be constructed with much faster response, but thus far industry has not made that demand.

Earlier chapters in this book have dealt with the theory of infrared absorption spectroscopy and its chemical significance. Chapter 3 on laboratory spectrophotometers discussed many of the conventional instrument components such as sources, optics, detectors, and amplifiers. We will address ourselves to the discussion of instruments and techniques which have been specifically developed or adapted for use in plant stream analyzers.

One thing the authors do not want to imply, in fact deny vehemently, is that a good plant stream analyzer can be constructed simply by placing a laboratory instrument in a box. The laboratory and plant stream instruments have different end uses, different requirements, and therefore different design criteria. Laboratory instruments have a multitude of controls since they must be versatile enough to solve many different problems. The plant stream analyzer is sensitized and adjusted to make continuous quantitative determinations of a particular component in a plant stream, week-in and

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week-out. The problem does not change: the composition of the plant stream and the analyzer readout do change.

Analyzer Requirements

What are the requirements of a plant stream analyzer? First, it must be able to solve the analytical problem. This includes the need for adequate sensitivity to the component of interest, and either sufficient selectivity or the ability to compensate for interference. It must also be able to accommodate the sample, a point which will be dealt with later.

Second, it must perform the analysis accurately and reproducibly over extended periods. Analyzer accuracy is limited by the accuracy of the standard samples used to calibrate the instrument. Reproducibility is more easily determined by rerunning stable precalibrated standards at periodic intervals. Although it may be a simple operation to calibrate and readjust the analyzer at short intervals, it is not a desirable substitute for good reproducibility.

Third, the analyzer must be reliable. This factor strongly influences the design, as it should, because the analyzer is expected to function without failure for extended periods of time. To insure reliability, analyzers are housed in explosion-proof or dust-tight gasketed enclosures, and purged with dry instrument air to provide protection and minimize the effects of corrosive vapors. The number of moving parts is kept to a minimum, mechanical parts are sturdily constructed and securely attached. Electronic components are selected for long life and are conservatively operated. An example of a deliberate design difference is the source, which in most sophisticated laboratory instruments is a Nernst glower. However, it has an unpredictable, often short, life. Analyzers commonly use a nichrome helix heated to approximately 800°C which will last for years.

Fourth, the infrared analyzer should be easy to maintain. A regular preventative maintenance program is necessary, but sooner or later the analyzer will break down. When this occurs, rapid return to service is a primary concern. An instruction manual, built-in provisions for testing, and adequate test equipment are extremely desirable. However, nothing is a substitute for a well trained serviceman backed up by qualified technical personnel. The preventative maintenance program must be considered before the instrument breaks down. Unless the program is well conceived and carried out, the analyzer will be neglected and its performance will progressively deteriorate.

Sample Handling

The sample handling system is not a part of the analyzer proper, but it is an extremely important part of the analysis system. Sample handling

generally consists of physical conditioning to present a clean, compatible, flowing sample to the analyzer without excessive time lag. Many things must be considered in the design of a suitable system, for example, the sample temperature, pressure, solids content, viscosity, corrosiveness, etc. Each sample stream presents different specific problems, and the literature contains a host of articles dealing with general as well as specific problems.^{8,16,33} Schall¹³ has in fact listed 74 references to papers on sample handling. The cost of the installed sample handling equipment may rival the instrument cost, but one must remember, without a properly prepared sample the analyzer is absolutely useless.

Types of Analyzers

There are three general types of infrared plant stream analyzers currently in use: the nondispersive, dispersive, and bandpass interference filter instruments. In addition there are many subdivisions and variations of these types, each having specific advantages and limitations. This chapter provides a description of their operating principles, a knowledge of which is necessary for proper selection and utilization of them as analytical instruments.

NONDISPERSIVE ANALYZERS

All infrared analyzers have a source, sample cell, and detector, and include as one of the above, or as a separate item, a method of wavelength selection. The type called "nondispersive analyzer," as the name indicates, does not use prisms or gratings to obtain wavelength selection. Nor does it include instruments using optical interference techniques such as interferometers or bandpass filters. There are three varieties of nondispersive infrared analyzers:

(1) Total absorption analyzers^{12,18,20} which measure the total infrared absorption by the sample.

(2) Negative filter analyzers^{10,11,34,42,43} generally have two beams, and wavelength selection is obtained by removing specific spectral regions from one beam. A chemical compound which absorbs in those spectral regions, and is placed in both beams, removes more energy from one beam than the other. This differential absorption is the basis of analyzer operation.

(3) Positive filter analyzers^{5,24,28,29,36,40,41} use a pneumatic detector which is filled with an infrared-absorbing gas. As energy is absorbed by the gas its temperature (and pressure) increases, and incident energy variations are sensed by observing changes in the pressure. Since the gas has an absorption spectrum the detector is only sensitive to energy changes occurring at specific wavelengths.

History

In 1870, John Tyndall used an infrared absorption apparatus which was the forerunner of today's nondispersive plant-stream analyzers. He used two sources, and thermocouple detectors in a dual beam arrangement having the sample cell in one beam. With this apparatus, total absorption was measured without differentiating between sample constituents. Eleven years later Bell⁶ and Tyndall³⁹ described the basic principles of a gas-filled detector similar to those used in today's positive filter analyzers. Very little was done in infrared analyzer development between 1881 and 1930 when Schmick³⁴ obtained a patent on an instrument which is remarkably similar to the negative filter analyzers in use today. Between 1930 and 1955, nondispersive analyzer development proceeded on all three types of instruments. Due to the inability of total absorption apparatus to discriminate between chemical compounds, they never gained widespread acceptance. Negative filter analyzers are capable of being sensitized for a single component in a rather complex stream. Although similar to Schmick's,³⁴ instruments developed by other workers have improved stability and sensitivity. The relatively high sensitivity of positive filter analyzers contributed to their receiving the widest acceptance of any of the nondispersive instruments.

In 1938 Pfund²⁹ patented an instrument which used a gas filled thermometer as the detector. In 1939 he described a detector using thermocouples, shielded from direct radiation, to sense the temperature rise of the enclosed gas.²⁸ However, it was 1943 when Luft²⁴ described a capacitor microphone detector which was basically the same as those used in all positive filter infrared analyzers today. Currently there are four companies in the United States, and at least three in Europe which manufacture this type of analyzer.*

It seems significant that most of the patents and publications on infrared analyzers were a result of work done by people in the chemical or petroleum industries. Indeed many of the commercial instruments were available as a result of licenses obtained by instrument companies.

Negative Filter Analyzers

Optics. The optical diagram of a typical negative filter analyzer is shown in Figure 13-1. A nichrome helix S is the source. Mirror M₁ collimates the beam which then passes through the sample cell Sa, to the beam splitter B. The beam splitter shown here consists of a series of narrow first surface mirrors mounted on a frame, and spaced so that the transmitted and

*Analytic Systems Co., Beckman Instruments, Inc., Gelman Instrument Co., and Mine Safety Appliance Co. in the United States. Sir Howard Grubb Parsons & Co. Ltd., Infra Red Development Co. Ltd., and Hartmann & Braun in Europe.

reflected energies are equal. The reflected beam passes through the sensitizing cell Se , to a plane mirror M_2 , a concave mirror M_3 , and is focused on the detector D_1 . The transmitted beam goes to plane mirror M_4 , through the compensating cell Co , to concave mirror M_5 , and is focused on detector D_2 . The purpose of the beam splitter is to divide the single beam in half to form sensitizing and compensating beams. The sensitizing and compensating cells are often called filter cells.

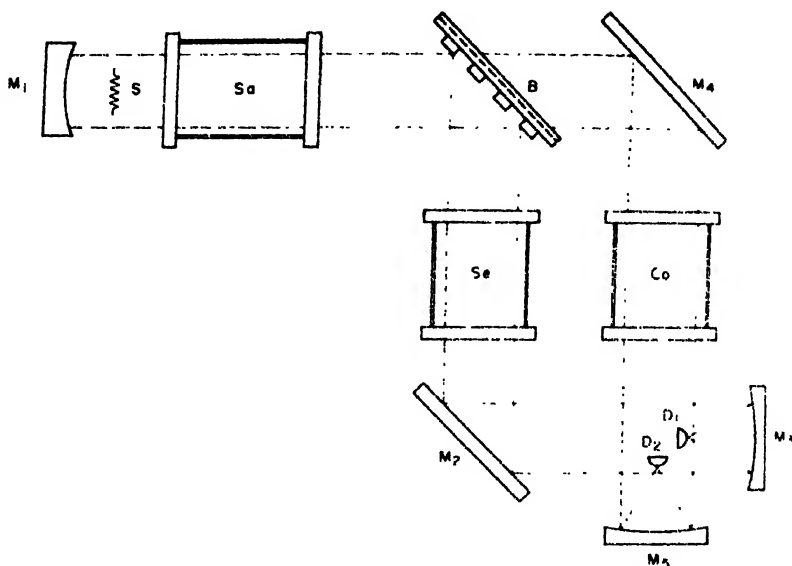


FIGURE 13-1. The Dow Chemical Co. beam splitter-analyzer optical diagram.

Detectors. The detectors used in this particular instrument are bolometers made by winding fine nickel wire on supporting forms. Their individual resistance varies with the integrated incident radiation. The detectors are electrically connected as two arms of a Wheatstone bridge, and a nulling servo recorder maintains bridge balance. The recorder indicates the difference in the two bolometer resistances which in turn depends on the difference in the two detector temperatures. The temperature of each detector is influenced by several factors, such as ambient temperature, bridge excitation current, thermal losses, and the total incident infrared radiation. The purpose of the analyzer is to determine the concentration of one stream constituent by measuring small differences in the total radiation incident on the two detectors.

Bridge Balance. The bridge, Figure 13-2, normally consists of manganin (low temperature coefficient of resistivity) resistors R , compensating resistors C_1 , C_2 and C_3 , detectors D_1 and D_2 , slidewire SW , slidewire shunt Sh , and transformer T_B . The amplifier A and motor M provide balancing action. The bridge is electrically balanced by shielding the detectors from radiant energy and placing manganin wire in the circuit, for example, as compensator, C_3 . The point of electrical balance is adjusted to be near midscale on the recorder. Optical balance is adjusted by inserting a mechanical trimmer in one beam until the optical and electrical balance points coincide. To insure stability two problems must be solved. Changes in ambient temperature or source voltage will cause drift unless carefully compensated.

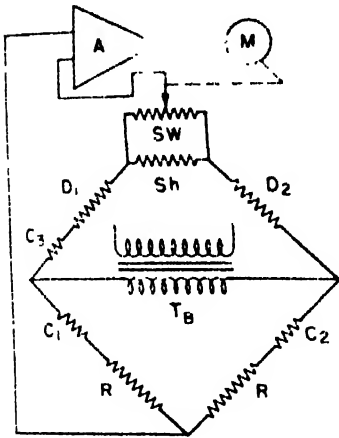


FIGURE 13-2. Negative filter analyzer electrical diagram.

Ambient Temperature Effects. Drift due to changes in ambient temperature is normally a result of differential detector temperature or detectors which do not have the same temperature coefficient of resistivity. In a typical bridge the resistance arms are balanced with 100 ohms in each arm, and the slide wire shunt is 0.03 ohm. A change of 0.06 ohm in the resistance of one detector causes full scale recorder deflection. A reasonable value for nickel's temperature coefficient of resistivity is $0.0045 \text{ ohm/ohm/}^\circ\text{C}$ at room temperature. Using these figures, one can calculate that if the maximum drift is 2% of scale, the differential temperature between detectors must be 0.00267°C or less. If the coefficient for one resistor differs by $0.0000012 \text{ ohm/ohm/}^\circ\text{C}$, a 10° change in temperature causes a 2% change in the recorder balance point.

In practice the differential temperature is not significant except when the ambient temperature changes rapidly (e.g., a door opened allowing a cold draft to blow on the instrument) or when a large thermal gradient exists

across the analyzer housing (e.g., the sun shines on one side of the housing). Of course both of the above examples point out the importance of analyzer location, and the advantage of insulating the housing. In addition, the detectors are mounted on a common thermal mass and carefully insulated.

Variations in the temperature coefficients of the bridge resistors are minimized by careful duplication of materials and fabrication technique, but in spite of precautions, compensation is necessary. This is accomplished without upsetting electrical balance by inserting a section of nickel wire in one arm of the bridge, for example, C_1 , and manganin wire in a corresponding position, for example, C_2 . The nickel wire is located close to the detector housing but exposed to analyzer temperature changes.

Source Voltage Effects. A change in source voltage and the concomitant change in radiated energy has two effects. First, it changes the temperature of the detectors, and if their temperature coefficients are different the bridge balance point will move. This is an effect similar to that encountered when the ambient temperature changed; however, since the compensating element C , does not sense the change in radiated energy it cannot act as a compensator. Second, the effective energy in the two beams changes differentially, hence, one detector is heated (or cooled) more than the other. This is a result of a combination of factors. One factor is the change in the spectral distribution of the source's radiant energy. The other factor is the deliberate dissimilarity in spectral make-up of the two beams which is a result of the sensitization procedure. One beam may be more sensitive to short-wavelength radiation than the other, and therefore the energy in one beam varies more with source temperature than the other.

Both effects of source voltage variation are simultaneously adjusted to zero by trimming the light on one detector and inserting (or removing) a manganin resistance in series with the other detector. It is important to note that this adjustment must be made after the analyzer is sensitized. The results of sensitization, particularly interference compensation, should be rechecked if significant beam trimming is required.

Sensitization. The sensitization of a negative filter analyzer is more an art than a science. Various methods have been suggested for reducing the number of trial and error runs,²¹ but it remains a task in which experience is a great ally.

Consider the analysis for methane in a sample stream containing methane, ethane, carbon dioxide and nitrogen. The sensitization procedure is shown in the sequence in Figure 13-3. Part I shows the blackbody radiation curve with nitrogen in both beams. Assume the beams are balanced with 10 units of energy in each beam. As shown in Part II, methane is placed in the sensitizing cell removing energy from that beam, and a mechanical trimmer is used to remove an equal amount of energy from the compensating beam.

When methane is placed in the sample cell, Part III, it diminishes the compensating beam energy. However, the sensitizing beam is not reduced since the methane in the sensitizing cell has already removed the energy absorbable by methane. The compensating beam now has less energy than the sensitizing beam, a condition called positive sensitization. The difference in energies is proportional to the concentration of methane in the sample cell.

When methane in the sample cell is replaced by ethane as shown in Part IV, both beam energies are reduced, but sensitization is positive. This is known as interference by ethane, and to remove the interference one balances out the positive sensitization with negative sensitization. The former was a result of placing methane in the sensitizing cell, and the latter is accomplished by putting ethane in the compensating cell. The mechanical trimmer is partially removed from the compensating beam to restore optical balance. The correct concentration of ethane for exact balance of positive and negative sensitivity, Part V, is found through trial and error. Ethane absorption bands do overlap those of methane to some degree so the analyzer's response to methane is reduced as shown in Part VI.

Introduction of carbon dioxide into the sample cell reduces both beams by equal amounts, and consequently its presence is not indicated by the recorder, nor does it alter the instrument's sensitivity to methane. The sensitization procedure resulted in the analyzer's having a positive response to methane and no response to ethane or carbon dioxide.

There is an important distinction to be made here. Negative filter analyzers record the difference in the energies incident on the two detectors. The process of sensitization results in a desired dissimilarity in the spectral energy distribution of the two beams. Sensitivity to methane depends on preferential absorption from one beam in the regions of dissimilarity, and is measured in terms of the energy difference caused by a given change in the concentration of methane. An equal reduction in the absolute value of the energy in both beams does not cause an energy difference, and consequently is not indicated by the analyzer. In addition, if the reduction occurred at wavelengths at which the beams were the same, the instrument's sensitivity to methane would not change. For instance, in the example, absorption by carbon dioxide would neither shift the balance point nor alter the sensitivity to methane. Dirt evenly distributed on the sample cell window would not shift the balance point, but would reduce the sensitivity to methane.

The example used was simplified to facilitate exploration of the basic concept. Considerably more complicated analytical problems have been solved using this type of instrument. However, increasingly complex problems require combinations of gases in the sensitizing and compensating cells. It is often necessary to complete a considerable number of trial and error tests before satisfactory results are obtained.

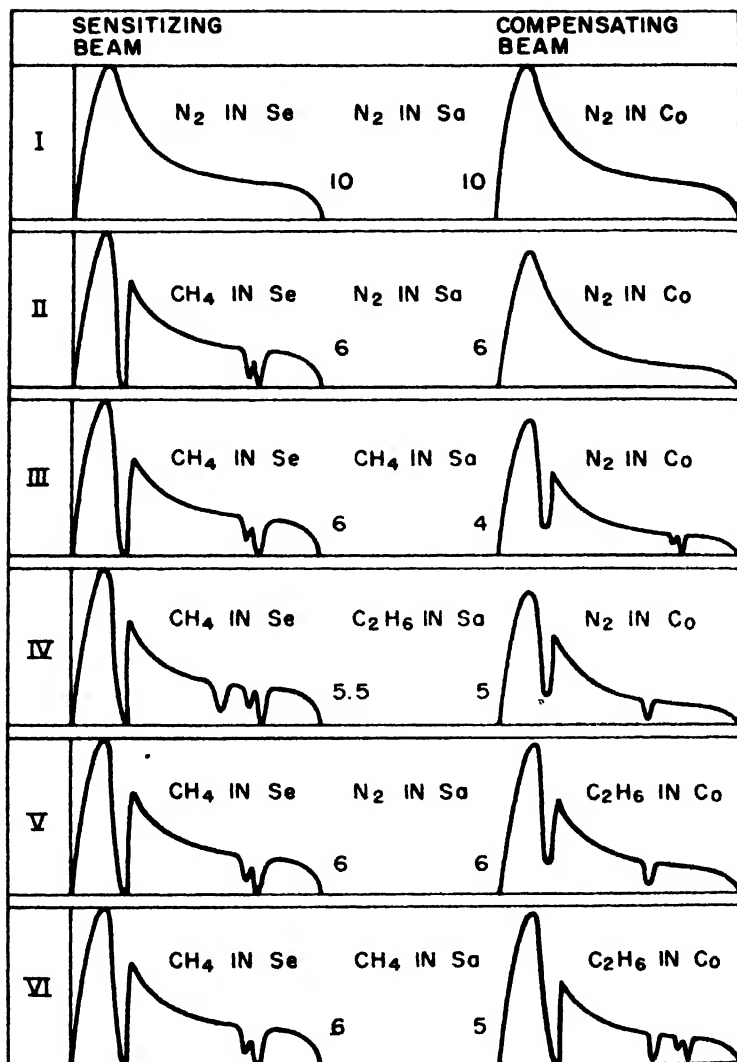


FIGURE 13-3. Negative filter analyzer sensitization procedure.

Substitute Sensitization. Substitute sensitization, as the name implies, is a technique in which an analyzer is sensitized by using a substitute chemical compound in lieu of the compound of interest. Such is obviously necessary when the analysis is for unstable, reactive, or extremely corrosive materials. This technique has also been used when the problem involves the analysis for a vapor having a low vapor pressure. Ammonia has been used to sensitize

instruments for water vapor analysis, since sensitization using water vapor would require an extremely long filter cell. This technique is more common in positive filter analyzers, for reasons which will become apparent.

Combination Sensitization. Combination sensitization is used when it is desirable to have the analyzer respond to more than one stream constituent. In our example, equal positive sensitization for methane and ethane could have been obtained by placing exactly the correct amount of the two gases in the sensitizing cell. This technique is often used on problems which call for purity determination, and the analyzer indicates total impurities. Although it has been used in positive filter analyzers it is more commonly associated with negative filter instruments.

Resolving Power. The spectral resolving power of a dispersive instrument is defined as

$$R = \frac{\lambda}{\Delta\lambda} \quad (13-1)$$

where $\Delta\lambda$ is the smallest difference in wavelength of identical spectrum lines that can just be discriminated, and λ is the average of the wavelengths (λ^1 and $\lambda^1 + \Delta\lambda$). According to the Rayleigh criterion, two lines are resolved when, in their diffraction pattern, the maximum of one falls on the first minimum of the other. A plot of diffraction patterns demonstrating the Rayleigh criterion is shown in Figure 13-4. At the point midway between the two maxima the intensity of each individual curve equals ~ 0.4 of its own maximum. The combined pattern shows two maxima with a minimum in the center and the intensity of the minimum is ~ 0.8 that of either maximum.

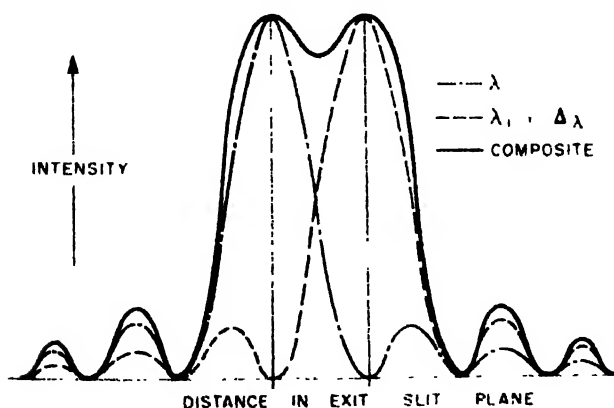


Figure 13-4. Diffraction pattern demonstrating the Rayleigh criterion of resolution.

The resolution of infrared spectrometers, particularly dispersive plant stream analyzers, is not diffraction limited, but is slit width limited. An intensity vs wavelength plot of energy passing through the exit slit, Figure 13-5, is symmetrically located about the wavelength which is centered on the slit. Application of the Rayleigh criteria leads to the conclusion that the limit of resolution is one half of the total wavelength interval passing through the exit slit. This is called the spectral slit width and for a grating instrument (assume a negligible diffraction term) is

$$\Delta\lambda_1 = \frac{sd \cos \theta}{fn} \quad (13-2)$$

where s is the slit width, d is the grating spacing, θ is the angle of diffraction, n is the grating order, and f is the collimator focal length. A more common way of expressing it for infrared instruments is

$$\Delta\nu_1 = \frac{\nu^2 ds \cos \theta}{fn} \quad (13-3)$$

where ν is the frequency in cm^{-1} ($\nu = \frac{1}{\lambda}$ where λ is in cm). Under normal operating conditions the spectral slit width for laboratory spectrometers is ~ 1 to 2 cm^{-1} , and, for dispersive plant stream analyzers, is ~ 10 to 25 cm^{-1} .

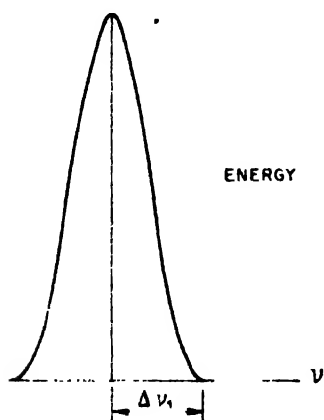


FIGURE 13-5. Energy passed by a spectrometer exit slit showing spectral slit width, $\Delta\nu_1$.

Now consider the nondispersive plant stream analyzer. Wavelength selection is a result of absorption by the sensitizing materials (chemical compounds). Assume a gas is used for sensitization and think of a single narrow band in its spectrum. The wavelength interval covered by this

absorption band can be compared to the wavelength interval of the energy passing through the exit slit of a dispersive instrument (twice the spectral slit width). In both cases, only energy at wavelengths within those intervals results in a change in the analyzer output. One can therefore consider the nondispersive analyzer to have resolution proportional to the width of the absorption band. The Rayleigh criterion is approximately satisfied if the limit of resolution of two identical bands is considered as occurring when

$$\Delta\nu = 1.2\gamma \quad (13-4)$$

where γ is the half-width, or width of the band in cm^{-1} between the half maximum absorption points as shown in Figure 13-6. Many rotational lines have half-widths ~ 0.1 to 0.01 cm^{-1} so the resolution of nondispersive analyzers may be several orders of magnitude greater than their dispersive counterpart. This is undoubtedly one reason for the success of nondispersive instruments on complex streams.

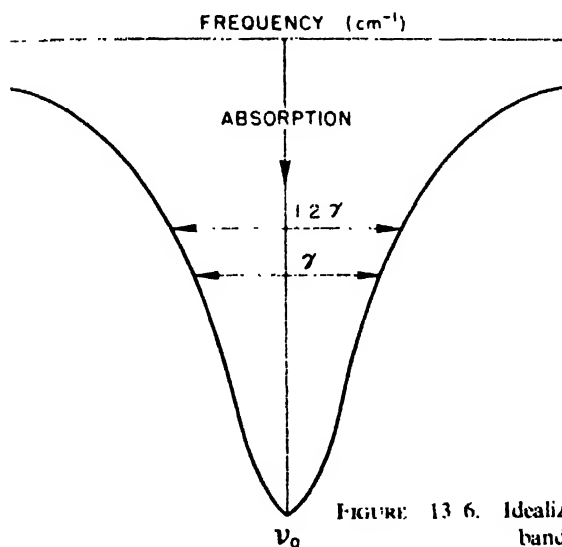


FIGURE 13-6. Idealized absorption band showing band half-width, γ .

There are several things which should be noted. First, the band half-width is a function of pressure and temperature. Its dependence on pressure accounts for the improvement in selectivity as the pressure of the sensitizing gas is decreased (higher resolving power). Second, the half-width of bands varies greatly with the chemical and particularly with its state. Band half-widths for liquids may be as narrow as $\sim 0.8 \text{ cm}^{-1}$ but are generally much wider, hence when liquids are used for sensitization the effective resolving power is much lower. Third, in any practical case there are a

multiplicity of absorption bands used in sensitizing the analyzer. In addition, many of the rotational bands of gases are so narrow that the band contours are not accurately recorded by laboratory spectrometers. These considerations lead one to conclude that the resolving power of nondispersive analyzers is a point to be understood but not calculated.

Commercial Availability. The only commercially available negative filter plant stream analyzer made in the United States today is sold by Leeds and Northrup Co., and is based on a design originally reported by Fastie and Pfund.¹⁰ It uses a nichrome source, tunnel optics, and differential thermopile detectors.

Advantages and Limitations. In the negative filter analyzers, large optical signals are incident on the detectors. Absorption by the gas of interest reduces one signal by a small amount, for example, 2%, and this small change in the large signal is expanded to full scale on the recorder. Satisfactory operation, therefore, depends on exacting thermal control or compensation and optical stability. However, these analyzers are simple, rugged, and have no moving parts. Where they can be used, they are ideally suited to industrial applications.

Positive Filter Analyzers

Optics. A typical arrangement for a positive filter analyzer is shown in Figure 13-7. Energy radiated from source S_1 forms the sample beam whose optical path proceeds past the chopper Ch, through the sample cell C_1 , the filter cell F_1 , to the detector D. Energy from source S_2 forms the reference beam and follows a similar path. The detector signal is amplified, synchronously rectified, filtered and displayed on recorder R. The sources are electrically heated to approximately 800°C. They should be matched so that a change in source current will affect both beams equally. The sample, reference, and filter cells have highly polished internal surfaces, and act as light pipes with infrared transmitting windows sealed on both ends. The chopper simultaneously blocks or passes both beams in a cyclic manner.

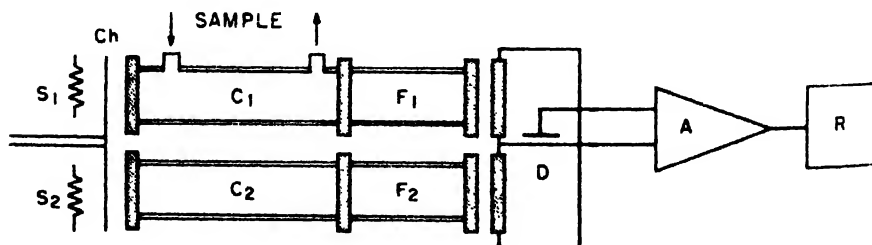


FIGURE 13-7. Typical positive filter analyzer.

Modulation of Selected Wavelengths. The use of a chopper and detection at that chopping rate presents another possibility, namely, that of modulating only the energy in a limited spectral region. This is accomplished by using various infrared transmitting materials in different portions of the chopper. In Figure 13-8, section 1 is generally metal and section 2 open, so that all radiated source energy is either passed or blocked. If one constructed section 1 of LiF and section 2 of CaF_2 , wavelengths below 4.5μ would always be transmitted and above 10μ would never be transmitted. Only the spectral region between 4.5 and 10μ would be modulated and thus contribute to the detector signal.

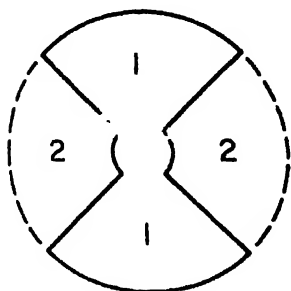


FIGURE 13-8. Chopper in a positive filter analyzer.

Detector. The heart of this type of instrument is the condenser microphone detector. It consists of two chambers filled with an infrared absorbing gas and separated by a thin metal diaphragm. Absorption of energy by the gas in the detector occurs only at wavelengths which correspond to the spectrum of that gas. If the amount of energy in the sample and reference beams is equal, then the temperature and pressure in the two corresponding chambers are equal and the diaphragm remains stationary. If the energy in one beam is diminished by sample absorption, a differential pressure and flexure of the diaphragm results. The magnitude of the diaphragm motion depends on the difference in the beam energies. To eliminate long term effects such as changes in ambient temperature, a small leak is provided between the two chambers, but the leak must not be large enough to reduce the pressure changes which occur at the chopping frequency. Proximal to the diaphragm is a metal plate which in conjunction with the diaphragm comprises the detector capacitor.

Detector Sensitization. Using a simplified theory of detector operation, Luft²⁴ obtained an expression for the change in detector capacity given by:

$$\Delta C = \frac{C(2r_1^2 - r_2^2)(K - 1)}{(\pi K P r_1^4 + 8 T V) D} \Delta Q \quad (13-5)$$

where

C	Capacity of detector at rest
r_1	Radius of the diaphragm
r_2	Radius of the fixed plate
K	Ratio of specific heats of the gas $\left(\frac{C_p}{C_v}\right)$
ΔQ	Energy absorbed by the gas
P	Partial pressure of the gas
V	Volume of one chamber
T	Tension of the diaphragm
D	Distance between the fixed plate and the diaphragm at rest.

Two factors in this equation deserve comment.

ΔQ is the energy absorbed by the gas in the detector when it is exposed to source radiation. Absorption is a function of wavelength, and the detector acts as an integrator over a given spectral region. ΔQ increases as the partial pressure of the detector gas increases. However, the spectral distribution of the absorbed energy changes with partial pressure. For example, consider a gas, A, which has large absorptivity and no interference at a wavelength λ_A . When the partial pressure of gas A in the detector is low, ΔQ is primarily a result of absorption at λ_A . As the partial pressure increases, ΔQ also increases, but the per cent from λ_A decreases. At some higher pressure all of the energy at λ_A will be absorbed near the entrance window, and contributes more to heating the window and less to the temperature rise of the gas as a whole. Analytical sensitivity is greatest when observing changes in sample transmittance at λ_A . Therefore, as the partial pressure of gas A in the detector increases from zero, sensitivity rises to a maximum and then declines. Luft²⁴ demonstrated this effect for detectors filled with carbon monoxide and with carbon dioxide. Maximum sensitivity to carbon monoxide was obtained with approximately 120 mm of that gas in the detector. For carbon dioxide sensitivity was maximized with approximately 70 mm of carbon dioxide in the detector. However, one must remember that the final choice of pressure will depend on both the selectivity and sensitivity requirements of the problem.

Equation 13-5 suggests another factor, $K - 1$, which should be considered. When a detector gas is used which has a ratio of specific heats (K) near one, the detector signal may be increased by adding a neutral gas having a relatively high ratio of specific heats, such as argon. V. N. Smith¹⁶ has compared detector outputs using *n*-butane and *n*-butane plus argon in detectors, and found the output signals could be increased as much as a factor of four by the addition of argon.

Any motion of the diaphragm is sensed as a change in detector capacity. In addition to the change caused ultimately by absorption there are several other sources of variation. Brownian motion of the gas molecules is the theoretically limiting noise factor, but the actual limit is more likely to be mechanical vibration or noise from the first stage of amplification. The only two methods utilized for sensing a change in capacity are by observing the effect on a tuned radio-frequency circuit or by using the detector capacitor to couple a D.C. voltage into an electrometer amplifier.

Since these are all chopped radiation systems only the signal component at the chopping frequency is detected, amplified, and synchronously rectified. The synchronous rectifier and low pass filter give the system band-pass response characteristics, and a corresponding improvement in the signal to noise level. Details on electronics are beyond the scope of this chapter but can be found elsewhere.^{7,22,23}

Selectivity. The section on resolution under "Negative Filter Analyzers" applies as well to this type of instrument. Since gases are used exclusively for wavelength selection, the positive filter analyzer has relatively high selectivity. It is also apparent that care must be exercised to avoid contamination of the sensitizing gas. Particular attention should be paid to the cleaning and outgassing of the detector prior to filling it, and the use of high purity gases is common practice. Many detectors have provisions for the inclusion of special absorbing or reacting chemicals; for example, metallic sodium is often used to remove the last vestiges of water vapor from the sensitizing gas.

Instrument Variations. Many of the commercial instruments available today are improved versions of the basic analyzer. Instruments are designed in which the effects of source voltage changes, deposition of dirt on cell windows, and variations in amplifier gain are reduced. Infrared analyzers are available which use filtering, compensation, ratio recording, and null balance techniques to increase analyzer selectivity and useable sensitivity.

Optical null. One improvement commonly encountered is the application of the optical nulling principle to instruments of this type. An optical null is maintained by reducing the energy in the reference beam an amount equal to the reduction by absorption from the sample beam.

Woodhull, Siegler, and Sobcov^{35,41} described the "Tri-Non"* shown in Figure 13-9. This instrument uses a combination of positive filter, negative filter, and optical null techniques. The attenuator A, controls the energy in the third beam P_3 , which is chopped in phase with the sensitizing beam P_1 . Since the gas of interest is placed in the sensitizing cell S_s , the two beams P_1

*Originally developed by the Perkin-Elmer Corp. Now the property of Mine Safety Appliance Co.

and P_2 , are not equivalent in their spectral energy distribution. When the same gas is introduced into the sample, beam P_2 is reduced by absorption at wavelengths corresponding to the major bands, but P_1 is reduced at wavelengths corresponding to minor bands. If the attenuator was inserted in P_1 , it would further reduce the energy at wavelengths of the minor bands. Spectrally the sample and attenuator would have different effects. However, by having P_3 , and placing the attenuator in that beam, the action of the sample on P_2 and the attenuator on P_3 is very nearly the same. Actually, such extreme measures are necessary in very few cases. The use of three beams allowed the designers to take advantage of positive and negative filter techniques and provide a good spectral match between effects of the attenuator and sample absorption.

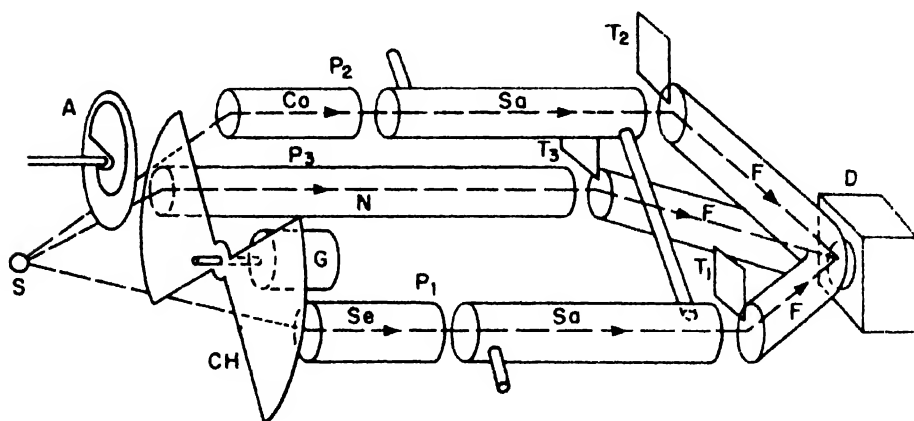


FIGURE 13 9. Optical diagram of the "Tri-Non" analyzer.

Waters and Hartz^{35,40} described an instrument in which optical nulling was accomplished by changing the temperature of the reference beam source. Absorption of energy from the sample beam activated a servo mechanism which reduced the voltage on the reference beam source until the energies were balanced. Negative filter techniques have been incorporated in this instrument, which is available from Mine Safety Appliance Company.

Ratio recording. A second variation is an electrical ratioing system used by Analytic Systems Co.³⁵ Two detectors are used, with one in each beam. The polarizing voltage on one detector is constant. The polarizing voltage on the second detector is variable and is controlled by the amplifier output. The amplifier input is the algebraic sum of the two detector signals, and the second polarizing voltage is automatically adjusted to reduce this difference

signal. Absorption by a sample stream constituent alters the ratio of the two detected energies and is reflected as a change in the ratio of polarizing voltages. Since the recording system has two detectors they can be filled with different gases, thus allowing compensation for absorption by interfering sample stream compounds.

Monobeam. The most recent variation in positive filter analyzers is the Beckman "Monobeam."⁵ It utilizes a single source, single sample cell, and two detectors in cascade. The two detectors can be filled with different gases or different partial pressures of the same gas. They are electrically connected so a difference signal is applied to the amplifier. The second detector can be used to provide compensation for optical interferences or to reduce the effects of dirt on cell windows. The use of negative feedback enhances the analyzer's stability.

Advantages and Limitations. Sensitivity and the ability to cascade detectors are the primary advantages of positive filter analyzers. They are commonly used to detect atmospheric or sample stream contaminants in the parts per million range. On the other hand, they are inherently sensitive to mechanical vibration, and lack the mechanical and electronic simplicity of the negative filter instruments.

DISPERSIVE ANALYZERS

Dispersive infrared plant stream analyzers are almost all of the "home-made" variety since very few instrument companies offer them as a standard item. Consequently there are almost as many different designs as there are instruments. We will try to describe several different types which we hope are representative of the many variations that have been built to solve special problems.

Dispersive infrared analyzers are characterized, of course, by their use of a dispersing element, either a prism or diffraction grating. They generally consist of a source of infrared radiation, a monochromator, and a detector sensitive to a broad range of wavelengths. The sample cell (usually for liquids) is placed somewhere between the source and the detector. The principal advantages of the dispersive analyzers over the nondispersive are: (1) a multicomponent liquid sample with a complicated spectrum may be analyzed for a specific component, (2) a proper sensitizing gas need not be found, (3) the problem of permanently sealing the sensitizing gas is eliminated, and (4) performance may be accurately predicted from laboratory spectra.

The spectral range usually covered by dispersive infrared plant stream analyzers is 0.7 to 25μ . The range 0.7 to about 3μ is referred to as the near infrared. If one can solve a problem in the near infrared rather than at

wavelengths longer than about 3μ , one is indeed fortunate. The following factors favor this spectral region:

(1) Commercially available and inexpensive glass-sealed lamps serve admirably as a source of near infrared radiation. These may be reliably operated at a higher temperature than an open source, thereby increasing and shifting the black body peak toward this wavelength region.

(2) Room-temperature lead sulfide photoconductive detectors may be used in this region. They are the most sensitive and inexpensive detectors available for this region.

(3) The near infrared represents the overtone region where molecules absorb radiation much less strongly than they do in the normal (fundamental) infrared region, allowing the use of cells with longer path lengths. This alleviates some sample flow problems.

(4) Inexpensive glass and quartz transmit in the near infrared and have good physical qualities making them ideally suited as optical materials. Unfortunately, however, the best specificity between absorption bands of chemically similar compounds (for example, isomers) is possible in the fundamental region of the spectrum. Hence, one cannot always operate in the near infrared since interference, due to the multiplicity of overtone and combination bands, may be a serious problem.

It should be pointed out that the single-component dispersive plant stream infrared analyzer is more than a laboratory spectrometer equipped with a flow-through sample cell that's been moved out to the plant. The difference, of course, is due to the fact that the laboratory instrument is a general purpose instrument. The dispersive infrared plant stream analyzer is constructed for optimum performance for every problem - there is no completely standard model. The wide variety of available components (see Chapters 5 and 7 of Ref. 17) permits and necessitates selection of the proper source, grating (blaze), transmission filter, cell windows, detector, amplifier, rectifiers, recorder, housings and sample handling equipment (which is itself a problem). The requirements of the particular measurement with respect to time of response, allowable noise, and sensitivity also affect the above choice of materials.

One Wavelength, Single Beam

One of the earliest dispersive plant stream analyzers is that of Herscher and Wright.¹⁵ Its optical diagram is shown in Figure 13-10. This is a single-wavelength single-beam instrument with the spherical collimator J used on axis in a Pfund²⁷ arrangement to fill out a NaCl prism E. Radiation from the nichrome source B is focused on the entrance slit F after reflection from plane mirror G. The radiation then passes through a hole in plane mirror K, is collimated, passes through the prism, is returned by the Littrow mirror

D, and the dispersed radiation passes through the hole in K and is focused on exit slit H. After reflection from plane mirror I, the radiation is condensed and focused onto a thermocouple detector M by spherical mirror N. A representative liquid sample continuously flows through the NaCl cell L. The radiation is modulated at 6 cps by the chopper C. The operating wavelength is determined by the angular position of the Littrow mirror D. The A.C. signal out of the detector is balanced against a generated 6 cps signal for an electrical null arrangement. The difference signal is amplified, synchronously rectified, filtered, and used to drive the balancing recorder. This minimizes errors due to amplifier gain changes.

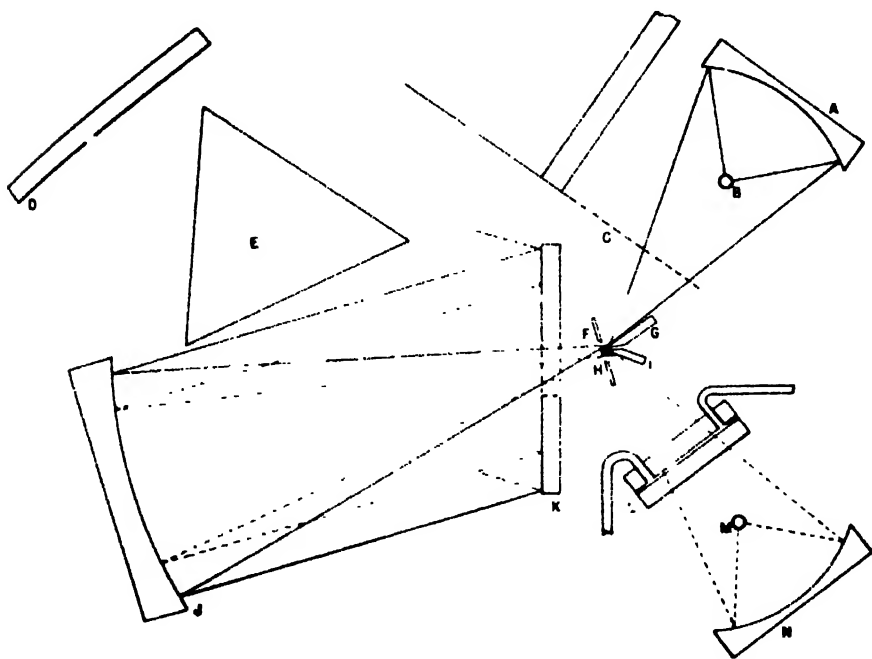


FIGURE 13. 10. The Dow Chemical Co. single beam, dispersive, infrared analyzer.

Instruments of this type are an improvement over nondispersive analyzers in wavelength specificity, but generally require frequent standardization. The output is affected by changes in the source emission, transmission of the cell (dirt, corrosion, fog), transmission and reflection of any of the optical components, and detector sensitivity. Analytically the measuring band must be free of interferences.

One Wavelength, Double Beam

Somewhat analogous to the development of laboratory spectrometers, plant stream analyzers of the double-beam type were built and successfully adapted to continuous process control problems. Most of these used the optical null method of obtaining the ratio of the two beams. In this system the detector is alternately illuminated by radiation which was passed through the sample (sample beam), and which was passed around the sample (reference beam). The detector output is an A.C. signal with amplitude proportional to the difference between the two beams. This signal is used to drive an optical wedge or attenuator into the reference beam until the two beams are balanced, or nulled. The position of the attenuator at balance is a measure of the ratio of the two beams. The optical layout is usually a miniaturized version of its laboratory counterpart. This system is a considerable improvement over the single beam in that source and detector variations do not affect the output. Changes in the common optical path usually affect each beam equally, and hence do not contribute to errors.

Except for sampling problems, plant stream analyzers are most frequently troubled with moving mechanical parts. The analyzer is expected to operate continuously, night and day and weekends for years without breakdowns. To eliminate the moving optical attenuator and still record the ratio of two beams, an instrument of the type shown in Figure 13-11 was developed.²

The instrument, whose diagram is shown in Figure 13-11 is a single wavelength, double beam, ratio recording type. It obtains a measure of the intensity of each beam by chopping each beam at a different frequency and separating the superimposed signals on a frequency basis. The ratioing of the signals is accomplished by the balancing action of the recorder.

The source of infrared radiation is denoted by S. The light from the reference beam source mirror (spherical) M_R is chopped at f_1 cps by the outer portion of the chopper C, passes through a focusing lens L_R , is reflected by plane mirror M_1 onto the monochromator entrance slits after losing one half of its light at the beam splitter B.S. (here being used as a beam-combiner). The light from the sample beam mirror M_S is chopped at f_2 cps by the inner portion of chopper C, is passed through the sample cell S.C. where it is attenuated due to absorption by the sample, passes through focusing lens L_S , and has one half reflected by the beam splitter B.S. to a focal point at the entrance slit F. The now combined beam is reflected by the plane mirror M_2 onto the spherical collimating mirror M_3 . The parallel light from M_3 illuminates the reflection grating G which disperses the light into a spectrum that is presented at the exit slit by spherical mirror M_4 . The angle of the grating with respect to M_3 , M_4 , and the slits,

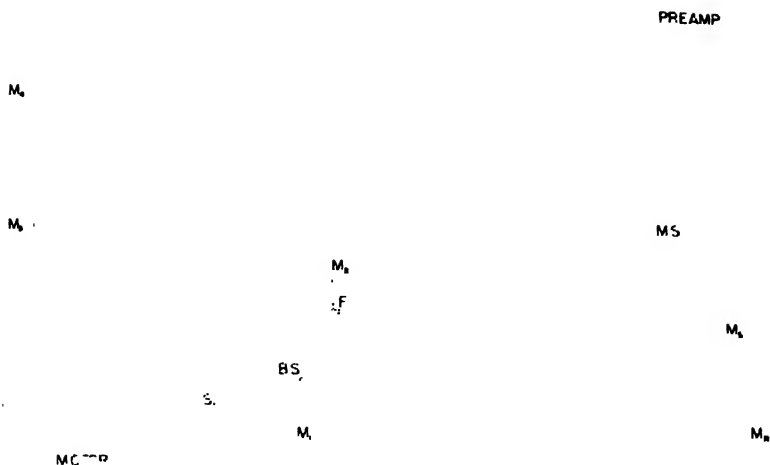


FIGURE 13-11. The Dow Chemical Co. double beam, electrical ratio recording, dispersive, infrared analyzer.

determines the wavelength that will be transmitted by the exit slit. Light of higher grating orders (shorter wavelength) is removed by the long-wavelength pass transmission filter *F*. The light from the exit slit is focused onto the detector *D* by lens *L*₂. The instrument of Figure 13-11 is designed for operation in the near infrared, hence the liberal use of lenses (inexpensive glass). The same result could be accomplished with reflecting optics only.

The electric signal from the detector consists of a superposition of the f_1 and f_2 signals. This signal is amplified and applied to two narrow band-pass amplifiers; one passes f_1 cps and the other f_2 cps. The bandpass amplifiers, in rejecting all other frequencies, accomplish the separation of the signals representing the sample and reference beam. To further discriminate against unwanted frequencies the two signals are synchronously rectified and filtered before they are ratioed in a recorder balancing circuit.

The rectifier contacts are sealed glass switches (normally open) actuated by a near-by magnet whose magnetic field is interrupted at f_1 or f_2 cps by an iron vane fastened to the chopper shaft. This arrangement has no frictional wear, the contacts are hermetically protected from corrosion, and the phase and timing adjustments remain constant for long periods of time.

This arrangement succeeds in reducing the moving parts to one rotating shaft supported by two bearings and still obtains a double beam ratio.

There is still one source of error, that of changes in the sample cell transmittance, for which the double beam method does not compensate, and which is far more serious in plant stream analyzers than in a laboratory instrument. With a continuously flowing process sample, the cell windows may under some conditions be affected by fogging, erosion, or corrosion. The sample background transmittance may change due to both solid and dissolved impurities, foam, or bubbles. It soon became apparent that a very powerful method of making an analyzer insensitive to almost everything but the absorption band being measured was to record the ratio of the intensity at two wavelengths, one the measuring wavelength at an absorption band, the other a nearby reference wavelength where the measured component absorbs little, if at all.

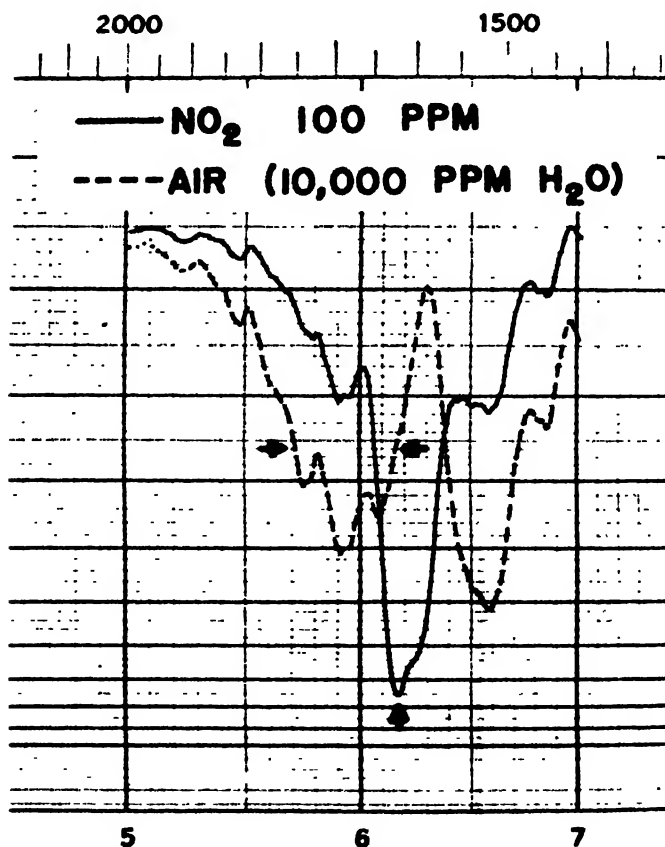


FIGURE 13-12. Portion of infrared spectrum of nitrogen dioxide and water vapor.

Two Wavelength

Recording the ratio of the intensity at two wavelengths yields an important bonus, in addition to rendering the instrument insensitive to energy changes due to factors other than sample absorption. The additional advantage is that the reference wavelength can be selected to eliminate also the effect of an interfering sample component which absorbs at the measuring wavelength. By selecting the reference wavelength such that the absorption due to the interfering component is equal at both wavelengths and recording the ratio, the output will be independent of changes in concentration of the interfering component. The effectiveness of this method is demonstrated in Figure 13-12 and Figure 13-13. In this problem it was desired to measure the concentration of nitrogen dioxide (0 to 100 ppm) in samples with varying water vapor content. A single wavelength measurement at 6.18μ would obviously be humidity dependent, but by recording the ratio of the 6.18μ output and the 5.7μ output, where water absorbs an equal amount, the instrument may be made completely insensitive to humidity changes. This is shown in Figure 13-13, which is a chart record

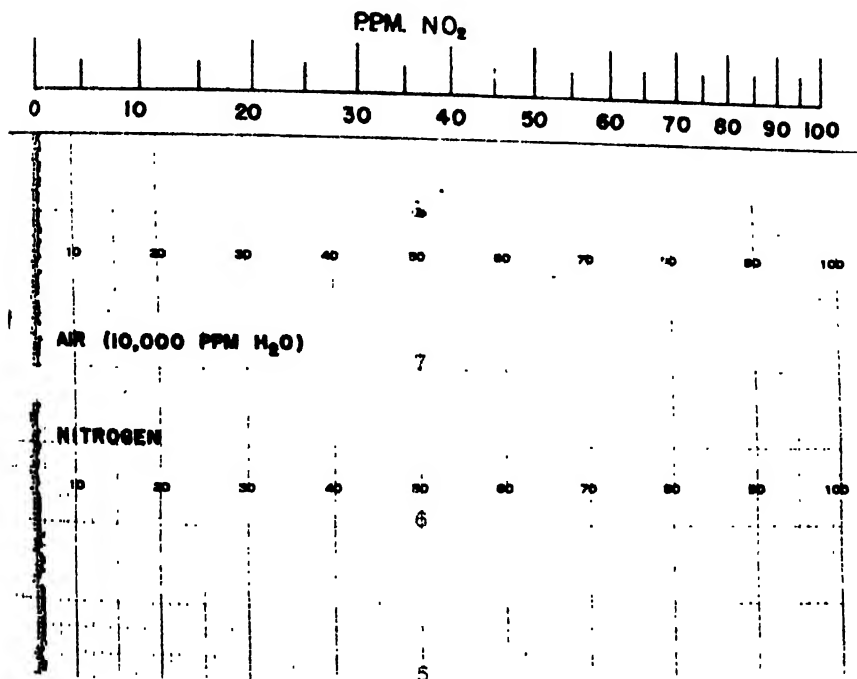


FIGURE 13-13. Chart record illustrating interference compensation capability of two wavelength, ratio recording, infrared analyzer.

of the output of this instrument for two samples; nitrogen containing a few ppm water and for air containing 10,000 ppm water.

The first dispersive plant stream infrared analyzer to use the two wavelength principle was the Perkin Elmer "Bichromator."¹² This instrument, now available only on special order from Mine Safety Appliance Co., is described with complete specifications in Ref. 35. Its simplified optical diagram is shown in Figure 13-14. Briefly, it obtains two wavelengths by using a split Littrow mirror with each half adjustable for individual wavelength selection. The chopper is arranged to alternately interrupt light eventually reflected by each Littrow. The A.C. detector signal, being proportional to the difference in intensity of the two beams, is used to drive an attenuator into the reference wavelength beam for optical null. The attenuator position, which is proportional to the ratio of the two beams (each beam containing light of a unique wavelength), represents the output of the instrument.

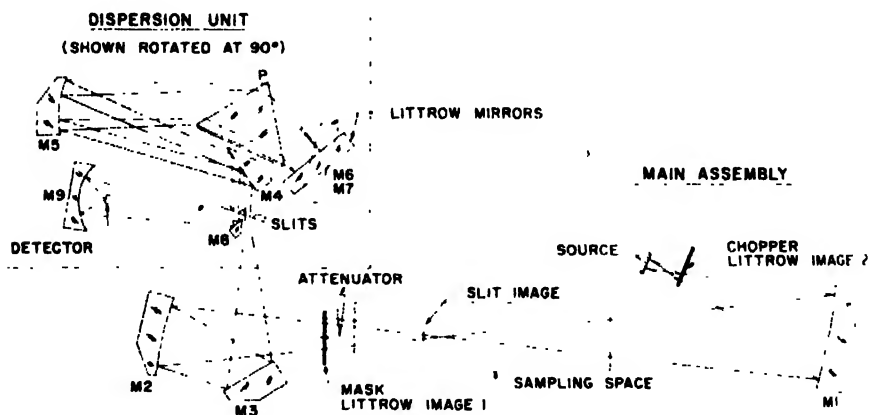


FIGURE 13-14. The "Bichromator" two wavelength, optical null, dispersive, infrared analyzer.

An instrument³ which obtains the same result as the Bichromator but by a different method is shown in Figure 13-15. This, too, records the ratio of the intensity at two wavelengths by means of optical null. Here the two wavelength output is achieved by illuminating the diffraction grating alternately with beams having different angles of incidence. The method is based on the well known grating equation

$$n\lambda = d(\sin i + \sin r) \quad (13-6)$$

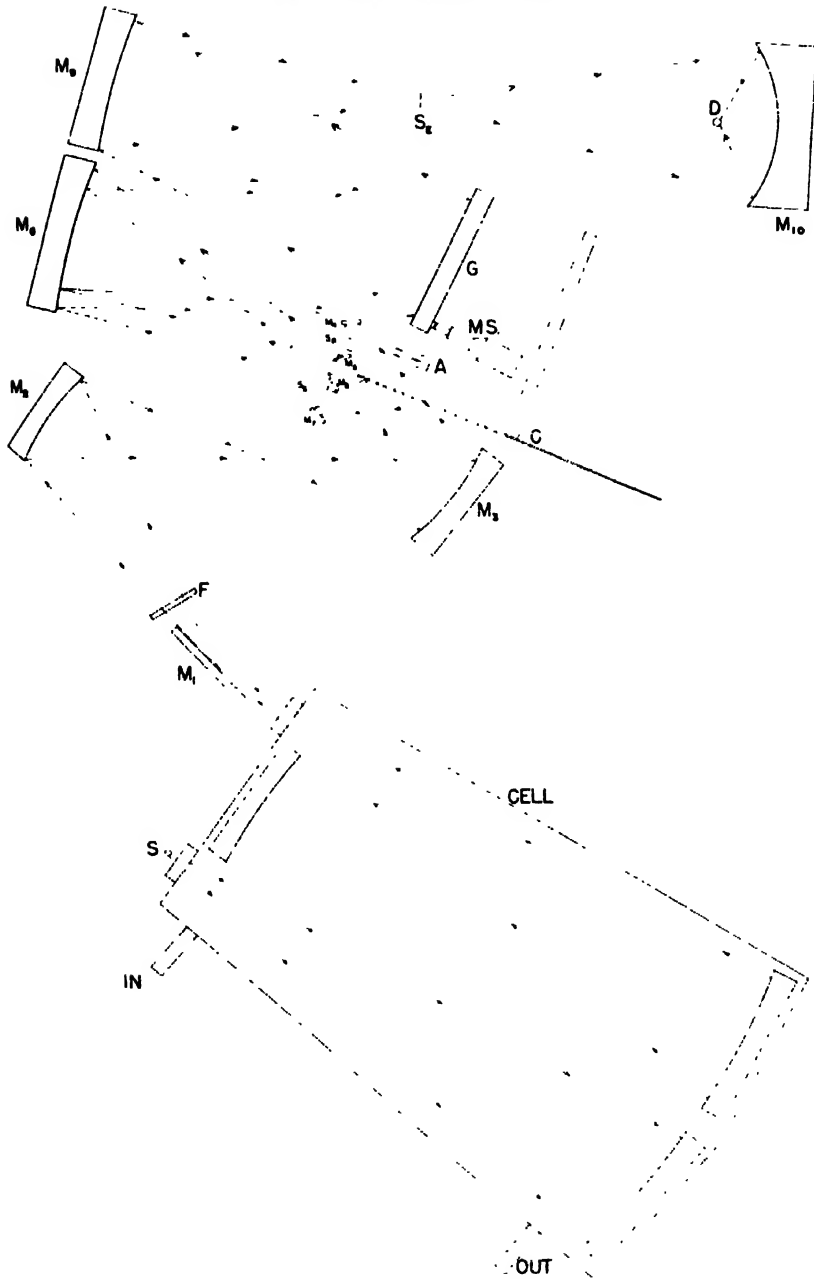


FIGURE 13-15. The Dow Chemical Co. two wavelength, optical null, dispersive, infrared analyzer.

where n the grating order (usually 1), d the grating spacing, and r the angle of diffraction, are held constant (one exit slit), and i the angle of incidence may have two values, permitting λ to have two corresponding values. The two angles of incidence are obtained by using two entrance slits alternately illuminated by a reflecting chopper. The wavelength of the light passing through one slit is determined (and adjusted) by the angle of the grating while the wavelength of the light passing through the other slit is proportional to the separation between the slits (this determines the difference between the angles of incidence of the two beams). The detector signal which again is proportional to the difference in intensity of the two beams is used to drive the attenuator A for optical null. This arrangement has a factor of 2 advantage in signal to noise over the "Bichromator" in that the entire aperture is used at each wavelength. The diagram (Figure 13-15) shows a long path folded cell being used with the analyzer for gas analysis requiring high sensitivity. This instrument is more frequently used with liquid samples in which case the cell is located between the exit slit S_e and the detector D.

An instrument which is identical in principle of operation to the one described above, but with the source and detector interchanged, is described in Ref. 9. This instrument uses one entrance slit and two exit slits, and focuses the light from each exit slit onto a single detector. An opaque chopper alternately chops the radiation passing through each slit, and the A.C. detector signal is used to null the reference wavelength beam with an optical attenuator. The optical attenuator is an interesting departure from the usual opaque comb or shutter. It is a wedge made of a semitransparent film on a rigid transmitting backing. This forces a larger portion of the beam to be used for balancing, thereby reducing the effects of nonuniform distribution of energy in the light beam. The transparency of the attenuator may also be chosen to give full scale travel for whatever transmittance change the problem calls for, thereby improving precision for high sensitivity applications. The instrument is designed primarily for operation in the near infrared where detectors have a large receiving area requiring little image reduction and no evacuated housing to make a dual exit slit with one detector arrangement practical. Where thermocouple or bolometer detectors are required, it is generally easier to use the source off axis to obtain two beams and use on axis optics with the detector. Also, if samples are at elevated temperatures, it is preferable to have the sample between the chopper and the detector so that radiation by the sample is not modulated by the chopper and hence not detected by the A.C. detection system.

Figure 13-16 is an optical diagram of an instrument⁴ which evolved as a combination instrument, using the two chopping frequency technique of

Figure 13-11 and the two wavelength by two entrance slits technique of Figure 13-15. The resultant instrument is one which records as its output the ratio of the intensity at two wavelengths, has the sample between the chopper and detector, and uses a rotating shaft as the only moving component in it.

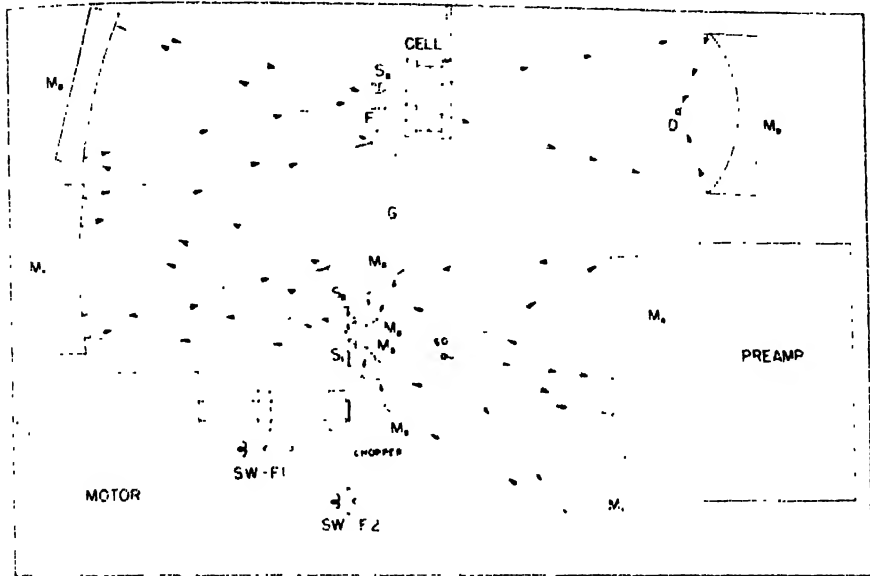


FIGURE 13-16. The Dow Chemical Co. two wavelength, two frequency, electrical ratio recording, dispersive, infrared analyzer.

The radiation from the source SO is formed into two beams, with a source image focused on each of two entrance slits. The light passing through each slit is chopped at two different frequencies, *not* alternately or with any special phase relationship relative to each other, but at frequencies chosen such that the combination detector signal may be readily separated by electric filters. The grating disperses the light from each slit into two spectra, displaced in wavelength, which are focused onto the single exit slit. The exit slit concurrently transmits light of each wavelength (and chopped frequency). The light, after passing through the sample cell, is detected by an appropriate detector D —thermocouple for wavelengths longer than about 3μ and a photon detector (lead sulfide usually) for shorter wavelengths. The detector signal, which contains both frequencies, is amplified in a common amplifier and applied to two tuned amplifiers (one for each chopping frequency) such that only the signal of a chopped frequency,

corresponding to one wavelength, is amplified, and the other frequency is strongly (50 db) rejected. The two signals are then synchronously demodulated by hermetically sealed relays (driven by a photo-duodiode actuated trigger circuit) filtered, and form the balanced input to a recorder circuit such that the recorder pen position is proportional to the ratio of the two signals. The wavelengths are selected for sensitivity and interference compensation as in the three previously described analyzers.

An interesting two wavelength dispersive analyzer, which is a great deal simpler than those described previously, is manufactured by the Grubb Parsons Co.²⁵ This instrument, called "The Spectrosorter," uses two narrow sources (actually two limbs of a U shaped wire) in place of, and at the same location as, the two entrance slits of the optical arrangement of the Dow instrument of Figure 13-16. The detector, a photoconductor, is so shaped and located as to act also as the exit slit. A diffraction grating is used as the dispersing element, a spherical mirror for the collimator, and a lens for condensing the spectrum onto the detector. A chopper alternately admits radiation from each limb of the source into the system. The detector signal, which is a measure of the difference between the intensities at the two wavelengths, is the output, indicated either by a meter or recorder. The output may be manually nulled for a given condition, say 0% concentration of the sample component being measured, by a beam trimmer. The instrument has several disadvantages, perhaps the most serious being the fact that the output is the difference rather than the ratio of the two wavelength beams, but was clearly designed for simplicity and low cost. The spectral range is limited by the sensitivity of the uncooled photoconductive detector -- about 7μ for the indium antimonide detector used. Resolution for a given grating is limited by the width of the source filaments and the detector. Wavelength difference between the two beams for a given grating and wavelength is determined by the distance separating the two limbs of the source.

Multi-Wavelength

The dispersive analyzers described to this point have all been capable of analyzing for only one component in a multicomponent stream. It is perhaps a natural extension to attempt multicomponent analysis by measuring several wavelengths either simultaneously or sequentially. While several laboratory spectrometers¹⁹ have been automated for multicomponent readout for repetitive samples, not many continuous plant stream analyzers have been so developed. Probably the greatest obstacle is the complexity of such an instrument which means that the cost of the original equipment will be high, components and subsystems must meet extremely rigid requirements to maintain overall reliability, and highly trained technicians are needed for subsequent maintenance and service.

The principal difficulty in having the instrument read out a multicomponent analysis in per cent concentration for each component is in signal handling or data reduction. All the spectrometer can do is measure the intensity at given wavelengths and slit widths. The detector signals at this point may be unuseable, however, since in a complicated chemical mixture several analytical absorption bands usually meet with interference by one or more of the other components. A computer (perhaps a simplified analog) is therefore required to solve the resultant set of simultaneous linear equations. The spectrometer with its flow-through sample cell and hot source must usually be placed in an explosion proof housing near the plant stream. The computer, recorder, and associated electronics must be located nearby and special provision made for protection against extreme environmental conditions, particularly corrosive vapors.

Ref. 1 describes a multi-channel infrared dispersive analyzer which provides a measure of the intensity at several wavelengths by using several detectors (photoconductive indium antimonide) placed in the plane of the focused spectrum of a prism spectrometer. The detectors act as their own exit slits, and the narrow source acts as the entrance slit for the spectrometer, using the conventional Littrow arrangement. The radiation from the source is modulated at 1.7 kcps by a cylindrical squirrel cage chopper. The indium antimonide detectors, while not as sensitive as a good thermocouple (at room temperature), have a much shorter time constant, hence may be used at higher chopping rates. This in turn permits the use of all-transistor amplification (since transistor $1/f$ noise is down) allowing a neat small package for the entire instrument. The analyzer was not applied to a particular problem but constructed to demonstrate the principles involved, so no data handling equipment was developed. A disadvantage of the multidetector approach to the multicomponent analyzer problem is that changes in the detector sensitivity with time or temperature are difficult to compensate for. An advantage is that no spectrometer elements (grating, Littrow mirror, slits) must be precisely repositioned for sequential repetitive operation. A somewhat similar instrument is described in Ref. 26, except that this is designed for the infrared range of 2 to 15μ , and uses thermocouple detectors and slits. The authors of Ref. 26 found that one detector per wavelength left something to be desired, and so developed an instrument which uses one detector for every two wavelengths and described it in Ref. 37. Here the radiation from two exit slits was focused on a single detector. The light passing through each slit was chopped at different frequencies permitting signal separation on a frequency basis by means of electric band pass filters. The optics become quite complicated and congested if this system is attempted for more than one pair of slits (wavelengths) and one detector.

Figure 13-17 illustrates a plant stream instrument which more nearly resembles a laboratory spectrometer than any analyzer described thus far. The instrument is a ruggedized, single beam, scanning spectrometer of limited spectral range with a minimum number of control knobs. The radiation from the source *S* is modulated by chopper *C*, dispersed by the grating *G*, and detected by the thermocouple detector *D*. *M*₁ to *M*₄ are spherical mirrors arranged conventionally. Scanning action is accomplished by rotating the grating by means of a cam and cam follower. A nearly constant *I*₀ is provided by programming the slits, again using an experimentally shaped cam. The wavelength and slit cams remain synchronized by being fastened to the same shaft. Since only one long-wavelength interference transmission filter is usually used to remove higher grating orders, the spectral range is normally restricted to the interval of the cut-on wavelength to twice the cut-on wavelength. The gratings are used in first order only; typical operating ranges are 8 to 16 μ and 10 to 20 μ . The sample may be either continuously flushed through the cell from the process stream, or manually injected. The output of the instrument is a plot of the single beam spectrum for a wavelength interval selected where the sample of

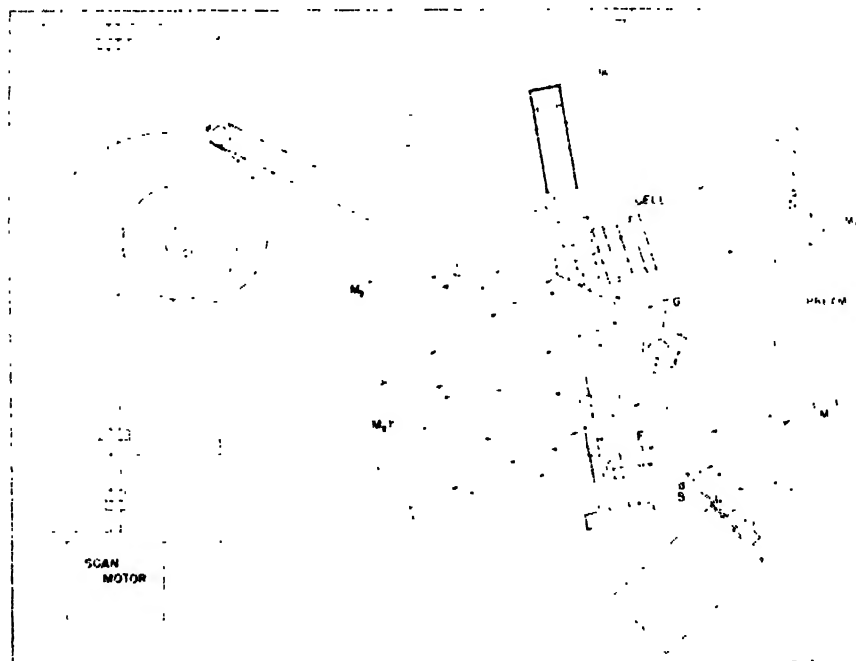


FIGURE 13-17. The Dow Chemical Co. repetitive scanning infrared analyzer.

interest has usable absorption bands. Scanning action may be either automatically repetitive or "on demand" by a push button. In either case, the strip chart recorder automatically stops during the reset portion of the scans. The recorder time record of the plant analysis is a series of spectra which the plant operator, or someone, must look at to interpret by comparison with a standard. The problem of data reduction is here avoided by using a human as the computer, but this is satisfactory where the data is completely routine and rather gross changes in the spectra are to be detected. This instrument is different from its laboratory counterpart mainly in ruggedness and reliability. It utilizes a purged explosion-proof housing for the spectrometer and purged, sealed cases for the electronics and recorder. The only controls on it are the I_0 adjust and the scan start button. The sample is used full strength. While this approach to multicomponent analysis demands a certain amount of training on the part of the plant operators, it is instrumentally very reliable and relatively inexpensive.

BANDPASS INTERFERENCE FILTER ANALYZERS

The relatively recent development of good, narrow bandpass, multi-layer interference filters has enabled the construction of several very promising plant stream infrared analyzers.^{13,31,38} These filters transmit radiation of a narrow wavelength interval only. The bandwidth (at half height) of the transmission band is typically 1 to 4% of the band center wavelength. They are available for any center wavelength in the usual infrared range but are infrequently used beyond 10μ where their band center transmission is down; band width is wide and cost is high since they are manufactured only with considerable difficulty for the longer wavelengths. Generally, the shorter the wavelength, the better the filter from a transmittance characteristic and cost viewpoint.

Nearly all of the infrared plant stream analyzers using bandpass filters use a two wavelength method to compensate for the usual changes inherent in single beam, single wavelength measurements. One of the first commercially available infrared plant stream analyzers using bandpass filters was the Analytic System Co. Series 500. This instrument, illustrated in Figure 13-18, was developed by the Shell Development Co. and is described in greater detail in Refs. 14 and 31.

The rotating filter wheel of Figure 13-18 alternately injects a filter into the light beam having a pass band at λ_1 , the measuring wavelength, and a filter having a pass band at λ_2 , the reference wavelength. Since the wheel is opaque between the filters, the detector output will be a series of pulses, with alternate pulses corresponding to the intensity of the reference and measuring wavelength. These pulses are amplified and separated by a

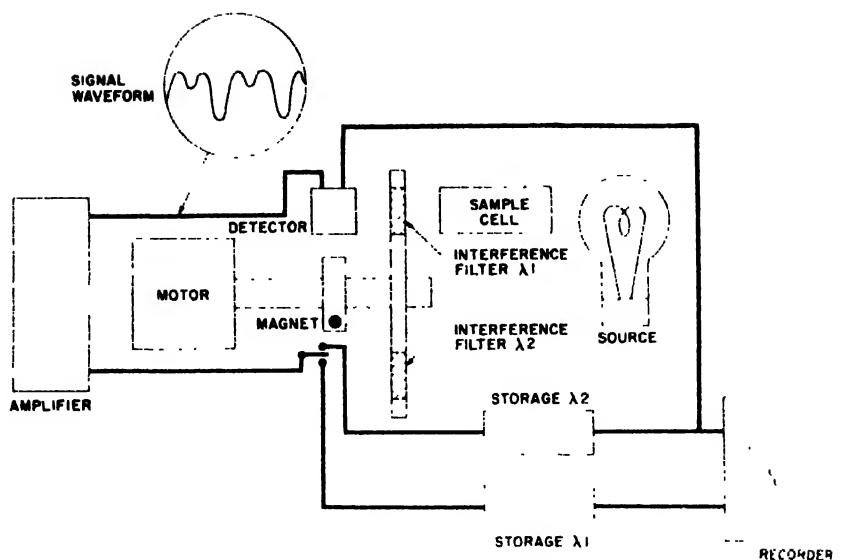


FIGURE 13-18. Analytic Systems Co. "Series 500" two wavelength, bandpass filter, infrared analyzer.

synchronously driven switch. Each separated signal is stored, while the switch is conducting the other, and the two signals are ratioed by the balancing action of the recorder. The signal levels are maintained at optimum values by an automatic gain control circuit which senses the reference signal level.

An instrument which is very similar in operating principle is the DuPont 800 Photometric Analyzer,³⁸ which at this writing is not yet commercially available. The optics in this instrument are so arranged that the sample cell is somewhat removed from the rest of the components, permitting use of a special cell capable of handling samples at 500 psi pressure and 200°C temperatures.

The bandpass filter analyzers have an advantage over the dispersive type in the near infrared in simplicity and cost. The principal advantage of the dispersive type is their superior resolution. This advantage looms larger as one goes farther out in wavelength.

OPTIMIZATION OF SAMPLE CELL PATH LENGTH

The sample cell path lengths used in plant stream analyzers are usually longer than those used in the laboratory for the same undiluted sample. There are several reasons for this, of which the most important is a consid-

eration of the factors which limit the ultimate obtainable precision. Beer's law states that for a binary mixture

$$T = e^{-c_1 a_1 l} e^{-c_2 a_2 l} \quad (13-7)$$

where c_1 , a_1 and c_2 , a_2 are the concentration and absorptivity (at a specified wavelength) of the sample background and component of interest respectively, l is the cell path length, and T the sample transmittance. Since $c_1 + c_2 = 1$, this can be written as

$$T = e^{-l c_2 (a_2 - a_1) - a_1 l} \quad (13-8)$$

The detector output is directly proportional to transmittance, but the quantity which is actually used and recorded as full scale recorder deflection is a voltage proportional to the change in detector output for a prescribed change in concentration of the measured component. The change in sample transmittance is related to the change in detector voltage, ΔV , by

$$\Delta V = k \Delta T \quad (13-9)$$

where k in a dispersive analyzer is a function of source brightness, slit width, aperture, dispersion of the grating or prism, and efficiency of the several optical components and detector. To make k as large as practically possible, all the components are selected for optimum performance (with other requirements considered as well) for a given problem, and the slits are widened to a maximum value. Frequently the slits may be widened until the image overfills the detector receiving area, and this should be done unless restricted by interference of a nearby band due to the resulting decrease in resolution. Assuming k in Equation 13-9 has been maximized and it is desirable to make ΔV as large as possible, for what value of path length, l , will ΔT be largest when c_2 changes by Δc_2 ? For a constant l , a_1 , and a_2

$$\frac{\partial T}{\partial c_2} = -(a_2 - a_1) l e^{-l c_2 (a_2 - a_1) - a_1 l} \quad (13-10)$$

$$= -(a_2 - a_1) l T \quad (13-11)$$

also, now holding c_2 , a_1 and a_2 constant

$$\frac{\partial(\partial T / \partial c_2)}{\partial l} = 0 \quad \text{for} \quad l = \frac{1}{c_2(a_2 - a_1) + a_1} \quad (13-12)$$

For this value of l

$$l = \frac{1}{e} \quad \text{or} \quad = 37\%$$

It is true that $\partial T/\partial c_2$ is greatest for l selected to yield $T \approx 37\%$ and, furthermore, ΔV has a maximum absolute value under these conditions. For the analytically easy plant stream problems where $a_2 \gg a_1$ and the change in c_2 is large, the path length is indeed optimally chosen to yield $T \approx 37\%$ for that value of concentration for which maximum sensitivity is desired. In practice the path length is made somewhat longer for sample flow reasons. This is permitted since the peak of $\Delta T/\Delta c_2$ (for constant Δc_2) vs l is a broad one.³⁰ Also when compared to laboratory data the band absorbance is reduced due to the lower resolution at which the plant stream analyzer operates. The apparent reduction in absorbance is compensated by increasing the path length; this is effectively trading energy for resolution, which for solely quantitative measurements is always a good bargain, since energy varies as the square of the slit width, and resolution as the first power.

The more frequently recurring problem in infrared plant stream analyzer applications is the more difficult one where a_2 is not particularly large, a_1 is significant, c_2 is normally zero, and a very small change in c_2 is to represent full scale on the recorder. Here the full scale change in transmittance is small, maybe 3% , even when l is chosen to make $T \approx 37\%$. The absolute change in transmittance for a constant change in concentration, hence in detector voltage, is still a maximum but one must examine the nature of the factors contributing to the errors in the final measurements before deciding on the optimum path length in this situation. The limiting factors are detector Johnson noise (a quantity independent of transmittance or signal size), and changes in the source emission, optics, sample (non spectral), detector sensitivity, amplifier gain, demodulator action, and recorder. While ratioing methods greatly reduce the effects of the above factors (except Johnson noise), no analyzer can completely eliminate them. Calling the factors listed above "measuring noise" for lack of a better term, and assuming it is the predominant noise (larger than Johnson noise), the best signal-to-measuring noise measurement is made where the ratio of $\partial T/\partial c_2$ to measuring noise is greatest. All of the contributing factors included in measuring noise are proportional to transmittance, or measuring noise = KT where K is a proportionality constant. Then from Equation 13-11

$$\frac{\partial T/\partial c_2}{KT} = \frac{-(a_2 - a_1)l}{K} \quad (13-13)$$

From Equation 13-13, the signal-to-noise is simply proportional to path length, but clearly this must be eventually limited by something. It is indeed limited by detector Johnson noise. The rule to follow for the high sensitivity application is to make the cell path length so long that the predominant

noise appearing on the chart is detector Johnson noise at a tolerable level. This is the optimum cell path length.

While the above discussion related, for simplicity, to a binary mixture, the results are the same for a multicomponent mixture. For the multicomponent case the c_1a_1 of Equation 13-7 represents the sum of the absorbances of the balance of the stream components.

These conclusions on optimum sample cell path length are based on absorption by a single band, having a single absorptivity. Nondispersive analyzers utilize absorption by a multiplicity of bands rendering impractical such a calculation. As a result, the length of the sample cell in those analyzers is ultimately determined by experience or by trial and error.

FUTURE TRENDS

As new materials are developed for general infrared use, they will continue to be applied to plant stream analyzers. Past examples include photoconductive detectors, interference filters, and cell window materials resistant to water, corrosion, and shock (mechanical and temperature) as, for example, the "Irtran" series by Eastman Kodak.

The latest devices, which will undoubtedly be applied to future infrared plant stream analyzers, are lasers, sublasers, and attenuated total reflectance cells. A sublaser as the gallium arsenide injection diode emits radiation of a narrow wavelength interval, capable of 100% modulation by changing the forward bias current, at frequencies in excess of 100 MC. This device can perform the functions of the source, chopper, and monochromator of the dispersive analyzer or the source and chopper-filter wheel of the band pass filter analyzer. And its total volume is about equal to a 1.4 watt resistor.

Attenuated total reflectance cells seem ideal for highly absorbing samples with flow problems since the absorption path length is independent of sample thickness. Probably the future infrared analyzer will utilize a combination of a monochromatic source, an attenuated total reflectance surface, and a detector, all packaged as a miniature unit.

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CHAPTER

14

Microtechniques Using Miniaturized Diamond Optics*

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H. C. Duecker***

INTRODUCTION

Although the infrared spectra of liquids and gases may be obtained by simple methods, obtaining the spectra of solids is sometimes difficult. Several special techniques have been developed for studying solids; of these, the technique chosen to study a particular specimen is usually dictated by the nature of the specimen. Each method, however, has certain disadvantages, either in sample handling or in the quality of the spectrum obtained. For this reason new techniques which either facilitate the study of solids or enable additional types of solid samples to be studied in the infrared region are always welcome.

A cell utilizing diamond or sapphire windows has been used to obtain the spectra of a wide variety of solids in the 2 to 35μ region. As far as is known, this cell may be used in a routine manner to study infrared spectra of all solids. The method is basically a microtechnique with which spectra of specimens weighing as little as $4\mu\text{g}$ ($4 \times 10^{-6}\text{g}$) can be obtained. The same cell can also be used throughout the visible and ultraviolet regions. Both solids and liquids, even extremely corrosive liquids, can be studied in the cell. Although the cell was originally designed to facilitate

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optical studies at high pressures, the ease with which spectra of solid samples could be obtained with this cell led to its use as a routine method for studying solids.

This chapter will describe the miniature diamond cell and discuss its application in infrared spectroscopy, at both atmospheric and elevated pressures. A microscope spectrophotometer developed to alleviate the problems caused by pressure gradients in the cell will also be described.

THE MINIATURE DIAMOND CELL

Description

The apparatus, shown in Figure 14-1, consists of the optical cell, its holder, and a mechanism for applying pressure. Two gem-cut diamonds with the culets ground and polished to form small flats parallel to the tables constitute the infrared cell proper. To minimize axial alignment problems, the diamonds are purposely ground to have different surface areas; the area of the smaller of a typical pair of diamond surfaces is about 0.5 mm^2 . Both square and irregular octagonal surfaces have been used. Each diamond is set in plaster of Paris with its tabular face resting in a close-fitting recess in a stainless steel piston. Each piston consists of two separate pieces, A and B, which are held together by screws. A centering post prevents the two pistons from rotating with respect to each other. A longitudinal hole drilled in the pistons allows the passage of radiation. The hole is cylindrical

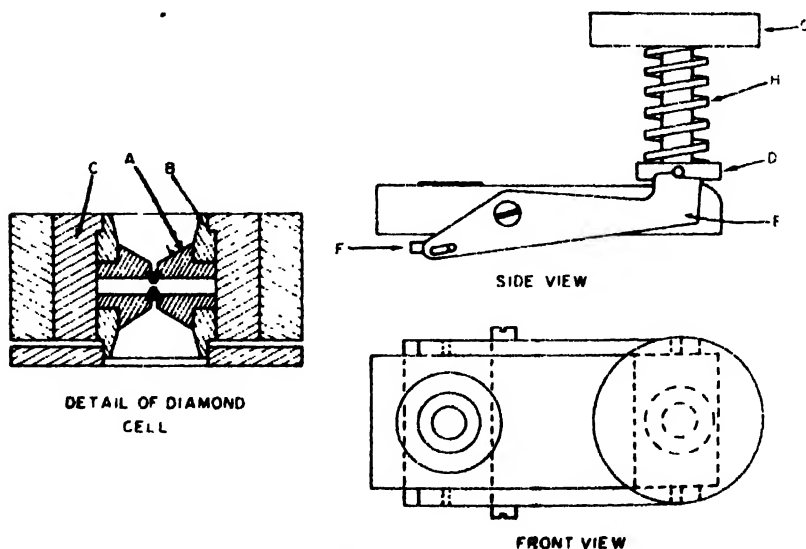


FIGURE 14-1. Schematic diagram of the diamond high pressure cell.

for the first 1/16 in. from each diamond table and then tapers outward to permit acceptance of the maximum flux from a cone of radiation which passes through both pistons, the diamonds, and the specimen contained between the diamond surfaces. The specimen itself is located at the focus of this beam.

The pistons slide in a hardened steel bearing, C, that fits tightly in a cylindrical hole in the steel block which carries the pressure generating equipment. One piston rests against a narrow flange at one end of the bearing. A presser plate, F, bears against the other piston. The presser plate is connected to a lever E that is pivoted in the steel block and actuated by a calibrated spring, H, which bears against the upper end of the lever. The spring is compressed by means of a manually operated screw, G. Channels surrounding the diamond cell can be drilled in the steel supporting block to allow circulation of liquids or gases for regulation of the temperature. Temperatures ranging from -30 to $+175^{\circ}\text{C}$ have been used. A small thermocouple may be inserted through one piston and placed in contact with the diamonds for temperature measurement. The whole unit is designed to be mounted in the restricted focal area of the lens system of a commercial infrared beam condensing unit. The functional parts of the cell are only 1 in. thick.

Cell Material

Natural diamonds may be classified into two main categories known as Types I and II, which differ in their transmission properties. Figures 14-2 and 14-3 compare the infrared spectra of the two diamond types. In the thicknesses used in our work (approximately 1/8 in.) both types of diamonds show intense absorption in the 4 to 5μ region with weaker absorption in

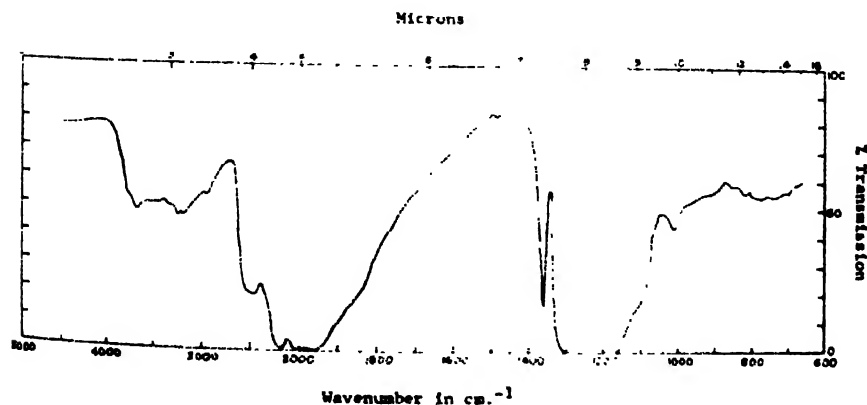


FIGURE 14-2. Infrared spectrum of typical Type I diamond, 3/32 in. thick.

the 3μ region. The Type I diamond shows additional strong absorption in the 7 to 10μ region. Both types are transparent in the 15 to 35μ region. For use as infrared window material the Type II diamond is required, since it is transparent in the important "fingerprint" region of the spectrum. The absorption in the 4 to 5μ region is undesirable, but, fortunately, relatively few characteristic group frequencies lie in this region. Thinner diamond windows (1 mm or less) are partially transparent in this region (see Figure 14-3), and spectra can be obtained if the diamond absorption is subtracted. To obtain spectra routinely in the 4 to 5μ region, the diamond windows can be replaced by sapphire windows. Through the use of these two window materials, the spectrum of any solid may be recorded from 2 to 35μ . If studies at elevated pressures or over a wide temperature range are to be made, the Type II diamonds are required, since they are capable of withstanding extremes of temperature¹⁶ and pressure⁴⁵ without noticeable change in transmission.

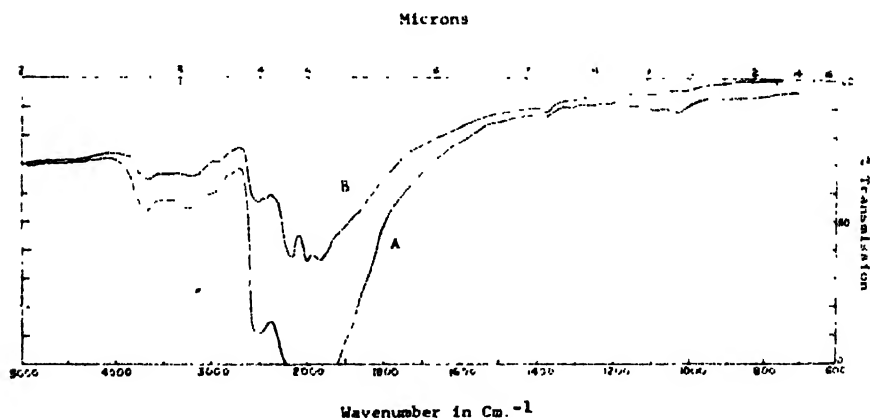


FIGURE 14-3. Infrared spectra:
(A) Typical Type II diamond, $3/32$ -in thick.
(B) Thin Type II diamond, 1 mm thick.

The distinction between Type I and Type II diamonds is not always as definite as implied by Figures 14-2 and 14-3; many sub-classifications which show differences in absorption in the 7 to 10μ region are recognized. The differences found in the absorption properties of diamonds have not yet been satisfactorily explained.¹⁶

Sample Handling

The sample handling techniques required when the diamond cell is used are very simple. No preliminary work need be done. The following procedure is used to obtain the spectrum of a solid:

One of the pistons is inserted in the bearing with the unit in a horizontal position. A small quantity of the specimen is placed on the diamond with a small spatula. An excess of sample on the diamond surface is usually not a problem, because any excess is readily extruded. The second piston is inserted, and hand pressure is applied to form an even film. The presser plate is then moved into place, and the pressure is raised to a few thousand atmospheres to obtain a clear film. Before the spectrum is recorded, the pressure is decreased to the lowest value consistent with maintaining a clear film, usually 1 to 100 atmospheres. The cell is then placed at the focal point of the lens system, and its position in the beam is adjusted to produce maximum transmittance in a spectral region containing no strong bands.

The total amount of sample required depends on the skill of the operator in placing the material on the diamond. One-half milligram is usually more than enough, and $10\mu\text{g}$ (10^{-2} mg) or less of material can be utilized by careful handling.⁴⁶

If absorption is too great for a given specimen, the sample may be diluted with Li^+ or KBr . For quantitative analysis the sample may be mixed and ground with a known weight of a suitable substance that has known absorption bands to serve as an internal standard. Increasing the intensities of weak bands is more difficult, but can be accomplished in some instances by repeatedly building up the film thickness, reducing the pressure of film formation, or, if necessary, increasing the diamond surface area.

When the spectrum is to be studied as a function of pressure, the pressure is repeatedly raised and lowered until sample extrusion ceases. Fortunately, the sample thickness remaining (on the order of 15 to 20μ) is usually sufficient to yield a reasonably characteristic spectrum. When extrusion has ceased, spectra are recorded, beginning with the maximum pressure. The changes occurring in the spectrum under these conditions are usually reversible. The reproducibility of the spectra and the lifetime of the diamond anvils depend greatly on the proper alignment of the anvil surfaces prior to each run. To facilitate alignment, part B of each piston has been equipped with small leveling screws with which the position of the parts A can be changed. Before the sample is placed between the diamond surfaces, the two diamonds are placed in position and observed in transmitted white light with a microscope focused on the anvil contact surfaces. The leveling screws are adjusted until white light interference fringes appear. Further adjustments are made until the number of fringes is minimized and the fringe system is centered on the surface of the smaller diamond.

Spectra of liquid samples can also be obtained with the diamond cell. A thin gasket made of aluminum foil or other suitable material with a hole smaller than the area of the diamond window is placed on the diamond surface. A drop of the liquid specimen is deposited on the diamond, and

the other piston is then inserted. Some of the liquid is extruded, of course, but usually the amount remaining is sufficient to obtain a reasonably good spectrum. The amount of liquid used can be varied by changing the thickness of the gasket.

Growing Single Crystals

A method^{14,72} has been devised for growing single crystals in the diamond cell. The liquid specimen, confined by a suitable gasket between the diamond surfaces, is subjected to sufficient pressure to cause partial crystallization. The pressure is then slowly released until only a single crystal remains in equilibrium with the liquid. (The process is observed by microscope.) With slight increase in pressure the single crystal grows until no liquid remains. The infrared spectra can then be obtained without difficulty. With this method workers at Battelle Memorial Institute have obtained infrared spectra of single crystals of benzene, hexane, sym-tetrachloroethane, sym-tetrabromoethane, and ethanol.

The benzene spectrum is shown in Figure 14-4. No spectral differences are evident between this high-pressure single crystal spectrum and those in the literature of low temperature single crystals.^{48,82} The possible resolution obtainable was demonstrated by a spectrum (not shown) in which the splitting of the 970 cm^{-1} band into a doublet was observed.

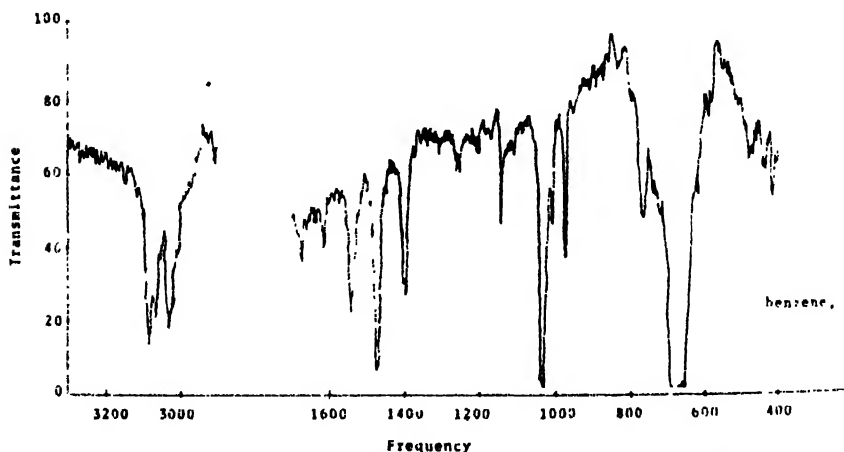


FIGURE 14-4. High pressure single crystal spectrum of benzene.

The sym-tetrachloroethane spectra shown in Figures 14-5 and 14-6 are particularly interesting. The liquid at room temperature is an equilibrium mixture of the *trans*- and *gauche*- forms. Low-temperature crystallization preferentially results in the *gauche* solid. All attempts to produce a low-

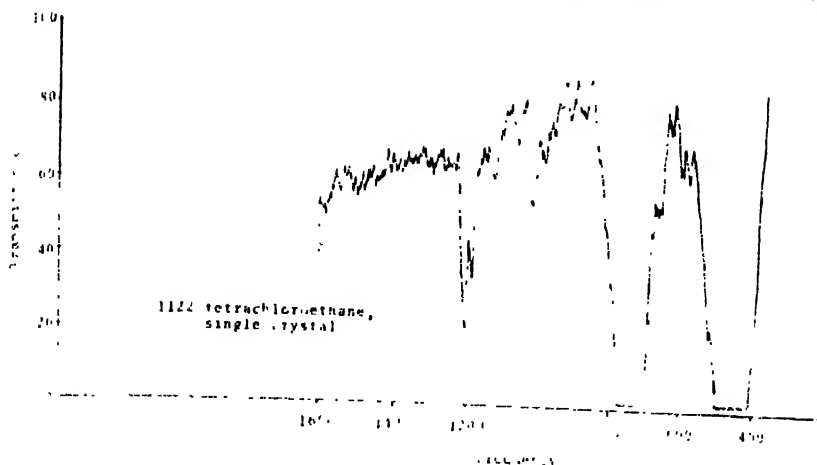


FIGURE 14-5. High pressure single crystal spectrum of *sym*-tetrachloroethane.

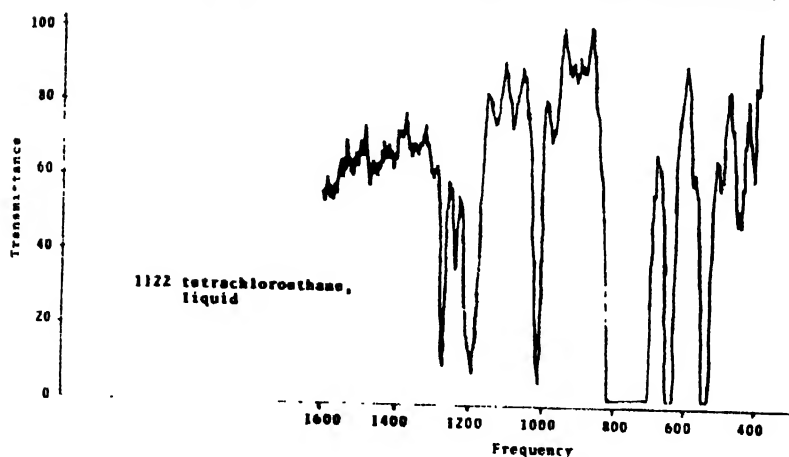


FIGURE 14-6. Spectrum of liquid *sym*-tetrachloroethane.

temperature *trans* solid have been unsuccessful. A comparison of the spectrum of the high pressure single crystal to that of the *gauche* solid reported by Kagarise⁷⁹ shows definitely that this single crystal is not the *gauche* solid. Although there are some discrepancies between this observed spectrum and that calculated for the *trans* form by Zietlow *et al.*,⁸¹ an examination of the liquid-solid spectral differences in *sym*-tetrabromoethane where the *trans* solid has been produced leaves little doubt that this is a single crystal of *trans-sym*-tetrachloroethane, and thus represents the first report of the isolation of this isomer.

Spectroscopic Equipment

The diamond cell can be used with most conventional Perkin-Elmer and Beckman instruments that are equipped with beam-condensing systems. Other instruments may require some modification. In this laboratory infrared spectra in the 1 to 35μ region have been obtained with the diamond cell using, primarily, a Perkin-Elmer 421 double beam spectrophotometer with a 6X reflecting beam-condensing system. When a Beckman infrared #4 spectrophotometer was used, the useful range of the instrument was extended to 35μ by replacing the KBr lenses in the beam-condensing system with KRS-5 (TlBr-TlI) lenses. The diamond cell has also been used with a

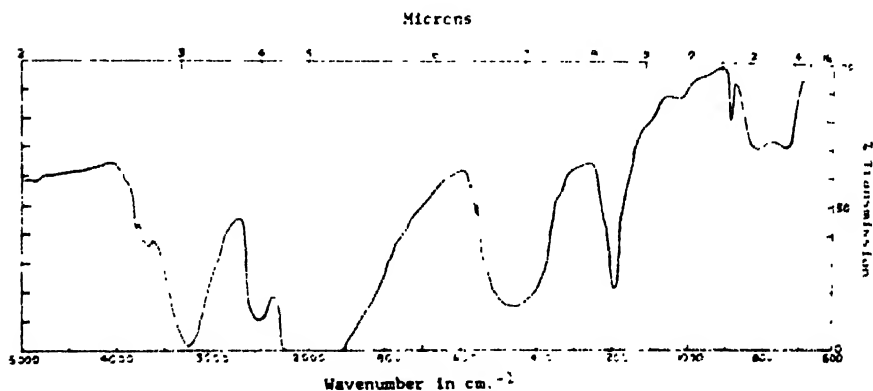


FIGURE 14-7. Infrared spectrum of boric acid-157.

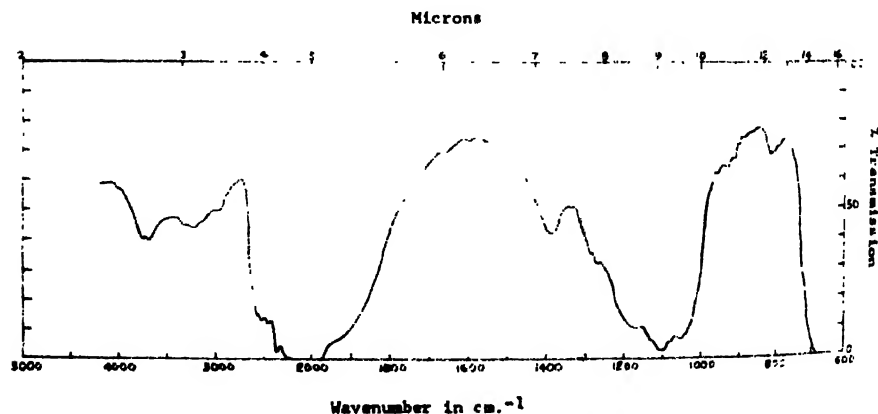


FIGURE 14-8. Infrared spectrum of cubic boron nitride.

Perkin-Elmer 350 and with a Cary Model 14 in the ultraviolet, visible, and near infrared regions. Careful selection of the diamonds is necessary for use in the ultraviolet region because not all Type II diamonds are transparent in this region.

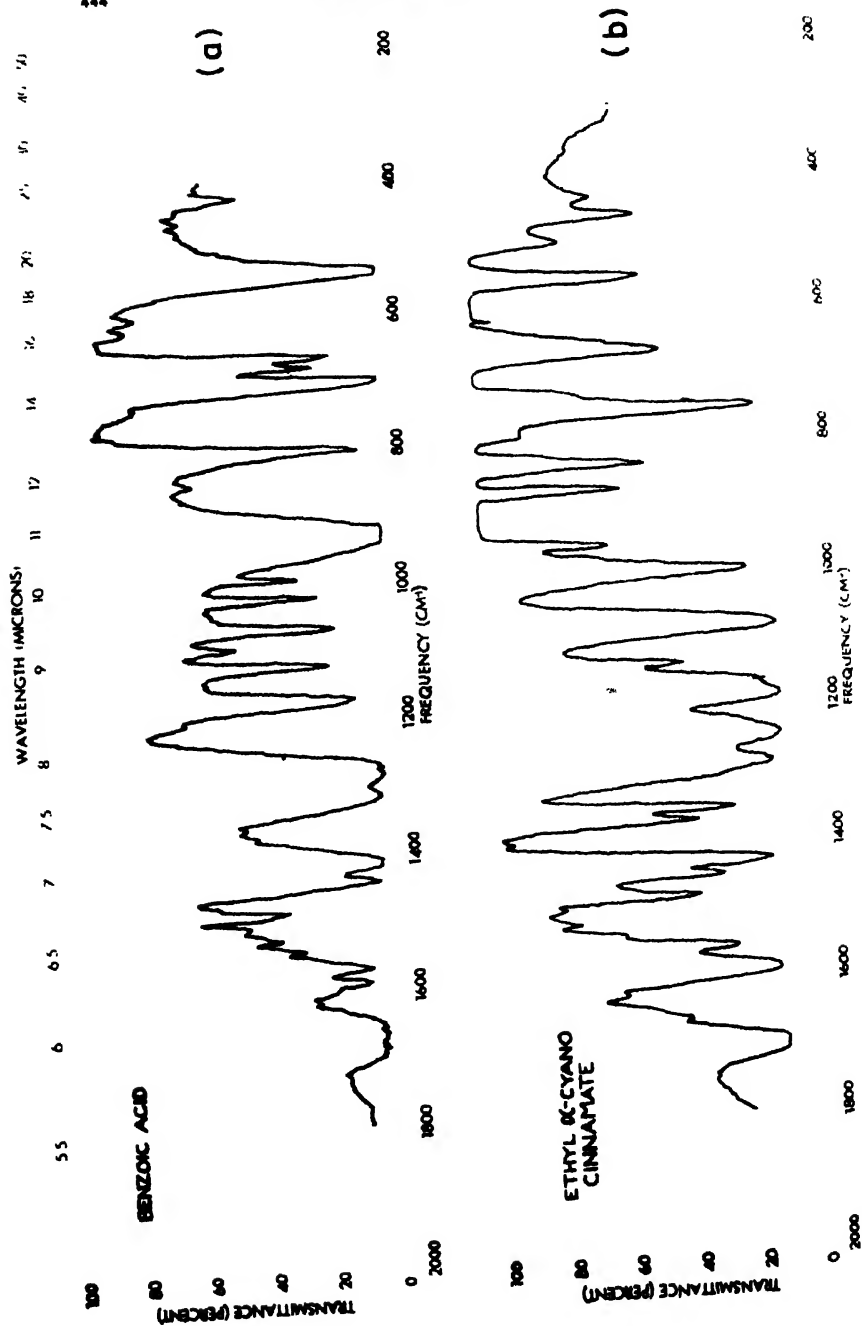
Since the aperture at the base of the diamond (see diagram of Part A of the piston) is approximately 2 mm in diameter, the full width of the focused slit is used, but the slit length is partially masked. To compensate for the resulting loss in available energy, so that the full scale of the instrument can be used, the reference beam is restricted by a wire screen or perforated sheet of aluminum. The limited amount of energy available makes slow scanning speeds desirable. Some typical spectra obtained on the Perkin-Elmer 421 with the diamond cell are shown in Figures 14-7 to 14-9.

APPLICATION OF THE DIAMOND CELL AS A ROUTINE METHOD OF OBTAINING INFRARED SPECTRA OF SOLIDS AND LIQUIDS

Advantages

With the diamond cell, spectra of solids and liquids can be obtained routinely, easily, and rapidly without many of the limitations inherent in other procedures. Preparation of the sample is extremely simple, and in most cases no preliminary work is necessary. Prolonged grinding, freeze-drying, and other time-consuming procedures are eliminated. Since the diamonds are inert, examination of reactive and relatively unstable materials presents no problems. Spectra of highly corrosive liquids such as fuming sulfuric and concentrated phosphoric acids have been obtained without difficulty with the diamond cell. The method is basically a microtechnique. Only small quantities of material are required, and no modifications are necessary to compensate for variation in the quantity of sample available. In addition, the specimen is unaffected by the experiment and can be recovered easily if desired.

In general, high quality spectra, consisting of sharp well-defined bands, are obtained with the diamond cell. No major interfering bands are present below 1800 cm^{-1} , so that the important fingerprint region is free of interference. When a spectrum in the region above 1800 cm^{-1} is required, a sapphire cell may be substituted. In most cases, the spectrum obtained with the diamond cell compares favorably with the spectrum obtained with a melt, mull, or solution specimen. Differences noted on comparison with good pellet spectra are usually minor, such as variations in the resolution and intensities of certain absorption bands, or the presence or absence of weak bands. Not infrequently, absorption bands which are unresolved by other methods are resolved by this technique.



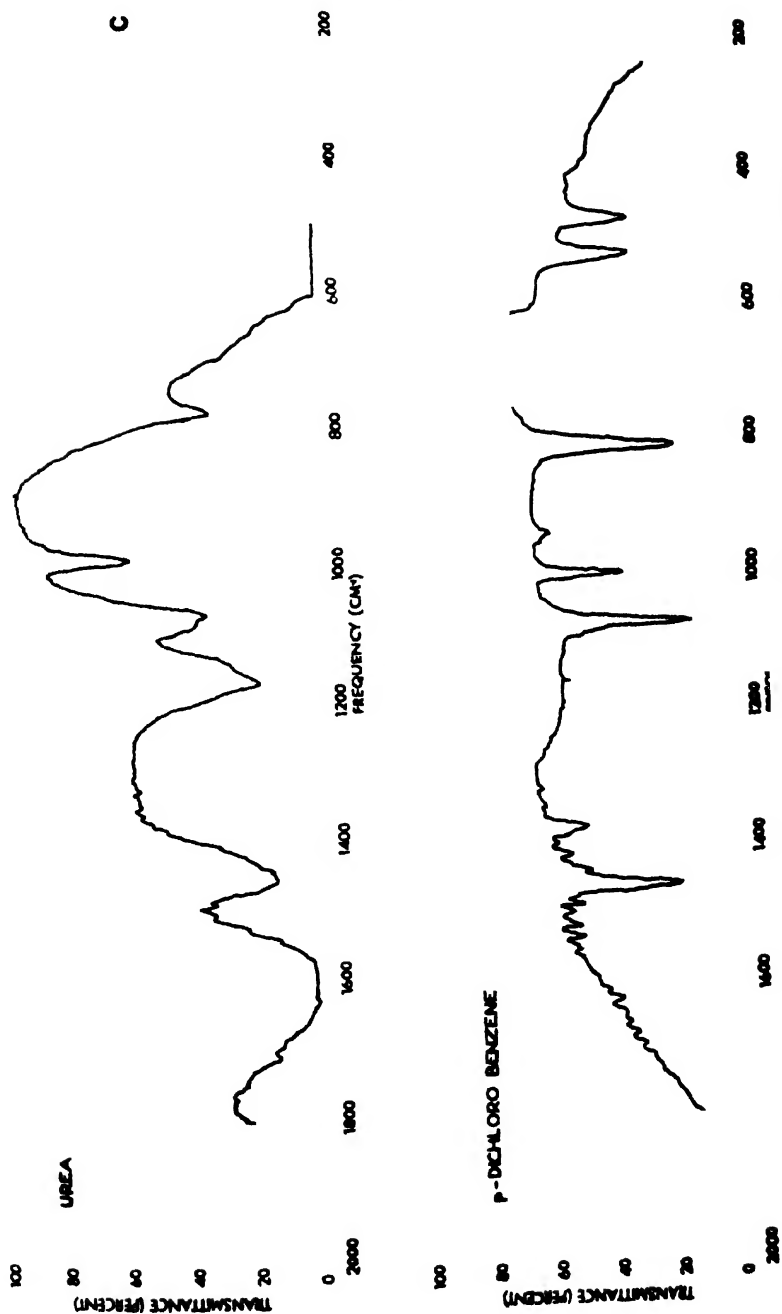


FIGURE 14-9. Infrared spectra of (a) benzoic acid (b) ethyl α -cyano cinnamate (c) urea (d) *p*-dichlorobenzene.

The diamond cell has, on at least one occasion, been used for a sample whose spectrum could not have been obtained by other means. Cubic boron nitride, a material as hard as diamond, cannot be ground by any ordinary means without introducing impurities. Ordinary pellet or mull spectra cannot be obtained because the index of refraction and/or particle size of the sample are too large. Solution and melting methods are inapplicable since retention of the cubic symmetry is important. A spectrum of cubic boron nitride has been obtained by using a small crystal crushed by the diamond anvils. An intense band at 1100 cm^{-1} has been assigned to the B—N str mode in the cubic form, and the band at approximately 700 cm^{-1} apparently corresponds to a bending mode.⁴⁶

In most methods of handling solids directly, problems of preferential orientation arise. Microscopic observation has shown, however, that specimens in the diamond cell are polycrystalline in nature with no apparent preferential orientation.

Disadvantages

The diamond cell technique does have a few disadvantages. The small surface areas of the diamonds necessitate the use of a beam-condensing unit. The diamonds have the strong absorption band that obscures the region from approximately 2400 to 1800 cm^{-1} and the bands of medium intensity near 3000 and 3500 cm^{-1} which can mask weak C—H and N—H frequencies. As mentioned above, all or part of these interferences can be eliminated by using thinner diamonds or sapphires. Spectra should usually be run under the lowest pressure consistent with maintaining a clear film since pressure transitions which may occur in some materials might cause unpredictable changes in the spectra. Transitions of this type are not widespread, and in most instances the effects of the transitions on the spectra are neither very marked nor irreversible.⁴⁵ Other pressure effects, such as shifts and intensity changes, are of such small magnitude at low pressures as to be negligible.⁴⁵

Internal Standards, Diluents, and Weak Bands

An internal standard is now required for quantitative work, but when an accurate method is developed for measuring the specimen film thickness, such standards will no longer be necessary. With normal specimen thickness some strong bands may show 100% absorption and some weak bands may not appear. This difficulty, however, arises in all techniques. If bands are too strong, an alkali halide diluent may be employed. Under these conditions, the diamond technique shares some of the problems of the pellet technique: the spectra may be altered by interaction of specimen and the polar matrix, and may be affected by polymorphism, differences in

grinding, and preparation conditions. These problems are less serious in the diamond technique because a 1 to 1 or 1 to 2 dilution with LiF usually suffices to reduce the intensities of most strong bands. Increasing the intensities of weak bands is more difficult, but can be accomplished in some instances by repeatedly building up the film thickness, reducing the pressure of film formation, or, if necessary, increasing the diamond surface area.

Comparison of Current Methods for Obtaining Spectra of Solids

To evaluate the usefulness of the method described here for obtaining the infrared spectra of solid samples, it should be compared with the other methods currently in use. The available techniques are listed in Table 14-1 along with comments about their scope of applicability, the quality of spectra obtained, and the ease of operation.

Miscellaneous Methods

The following miscellaneous methods have also been developed. Spectra have been obtained conveniently on solids squeezed between salt plates which contain a rectangular moat-type channel surrounding a transmittance region of 1 by 5 mm.⁶⁴ With this method a useful spectrum can be obtained with small quantities of sample, sample recovery is possible, and no interfering bands are present. The procedure, however, is limited to relatively soft solids and requires a beam condenser. Solids have been laminated with thin sheets of mica or silver chloride. Polyethylene sheets can be impregnated with various solid materials.⁶⁴ This method has the advantage that impregnation is effective with insoluble or nonplastic materials, but it has only limited applicability because of the polyethylene and mica bands which interfere with the sample spectrum. Suspension in suitable liquid media using emulsifying agents has been useful for some solids,²⁰ bacteriological specimens have been studied as dried films mounted on silver chloride windows,⁶¹ and a matrix isolation technique⁶ using low temperature Dewar systems with liquid He, H₂, Ar, N₂, CO₂ etc. has been developed. The specialized techniques and equipment required in the matrix method severely limits its use as a routine method.

APPLICATION OF THE DIAMOND CELL IN HIGH-PRESSURE STUDIES

Application of high pressures in microscopy and spectroscopy yields information about the nature of molecular interaction forces in a substance and about possible pressure-induced internal distortions of the molecules. The diamond cell has greatly facilitated optical studies at high pressures. Several devices have been constructed or adapted for use in high-pressure crystallographic or spectroscopic research, but the compact, versatile, and simply operated diamond cell is probably one of the most

TABLE 14-1. CURRENT METHODS OF OBTAINING INFRARED SPECTRA OF SOLIDS

Method	Scope of Applicability	Quality of Spectra Obtained	Ease of Operation	Ref.
Alkali halide disc	Applicable to large number of compounds. Quantitative methods can be used. Microquantities require beam condenser.	No interfering bands. Scattering effects are usually not observed. Interaction of polar matrix and specimen can cause significant changes in spectrum. Polymorphism, differences in grinding or preparation conditions, and use of different matrix material may cause differences in spectra. Particle size effects are occasionally observed.	Requires pressed disc techniques. Discs may be stored if sample is non-volatile and inert to matrix. Sample can be uniformly distributed. Adsorbed water can be troublesome.	1, 2, 5, 6, 10, 15, 17, 18, 23, 24, 28, 30, 32, 38, 40-42, 49-51, 53-57, 60, 65, 67-71, 77, 78
Mull	Applicable to large number of compounds Quantitative analysis requires internal standard.	Useful if proper techniques are followed. Fewer interfering bands than most solvents. Spectra may be affected by differences in grinding or method of preparation. Polymorphic changes may occur. Scattering, orientation, and Christiansen effects may be observed.	Sample preparation is simple. Sample recovery is difficult. Particle size may be important. Most common mulling agent: Nujol	3-5, 7, 11, 12, 23, 29, 37, 51, 56-59, 2, 63, 65, 68.
Solution	Applicable to large number of compounds within limits imposed by solubility conditions. Especially useful in quantitative analysis.	Compared to spectra of crystal state, solution spectra have broader bands and reduced intensity. Solvent bands may interfere. Interaction of solvent and sample may cause frequency shifts, new bands, and disappearance of bands	Sample is easily prepared with known thickness. 25 mcg or less of solid material may be used.	7, 37, 59, 62, 63, 65, 66

TABLE (4-1). CURRENT METHODS OF OBTAINING INFRARED SPECTRA OF SOLIDS (CONTINUED)

Method	Scope of Applicability	Quality of Spectra Obtained	Ease of Operation	Ref.
Single crystals	Applicable only when single crystals can be grown.	Sharp, well-defined bands. No interfering bands.	Procedure is time-consuming.	31
Solids crystallized from melts	Very useful for low-melting solids. Structural changes and decomposition may occur with substance of high m.p.	Sharp, well-defined bands. No interfering bands when compound is unchanged upon melting. Polymorphism may occur.	Preparation of sample is simple. Milligram quantities are required. Sample recovery is simple.	29, 62, 63, 66.
Deposits from vapor or solution	Special techniques may be required to obtain wide application (unusual solvents, low temperature cells, etc.).	No interfering bands. Scattering, polymorphism, and Christensen effects are sometimes observed.	Preparation is laborious. Optical reproducibility is sometimes difficult. Size of particle is important.	7, 19, 29, 59, 62
Miscellaneous See text. methods				

widely applicable.^{9,25,26,27,33,35,36,43,44,52,73,74,79} Attention in this section will be confined primarily to its use in the study of the effect of pressure on infrared spectra.

In general, a number of changes may occur in the infrared spectrum of a substance when pressure is applied: these include shifts of absorption bands from their positions at 1 bar, splitting of bands as the symmetry changes, appearance of new bands, and changes in band intensity. These effects may occur either discontinuously because of pressure-induced phase changes, or continuously because of a pressure-induced change in bond environment in a given phase. Except for substances involving systems of hydrogen bonds, the magnitude of the band shifts has ranged up to ± 10 cm^{-1} ; in hydrogen-bonded substances larger shifts are often observed. Changes in the apparent intensity of many bands are observed even at relatively low pressures, i.e. 10 kbar, with larger changes occurring at higher pressures. These intensity changes are specific with respect to both the nature of the substance and the mode of vibration involved. Several examples of pressure-induced spectral changes follow.

Examples of Pressure-induced Spectral Changes

The effect of a pressure-induced phase transition on the infrared spectrum of an ionic solid may be illustrated by the behavior of barium nitrate: the frequency of the out-of-plane bending vibration for the nitrate ion undergoes a discontinuous shift and splitting at the phase transition. The effects of pressure-induced phase transitions on the spectra of NaNO_2 , KNO_3 , AgNO_3 , ferrocene, ice, CaCO_3 , semicarbazide hydrochloride, and methylamine hydrochloride have also been observed with the diamond cell.⁴⁵⁻⁴⁷

Infrared spectra of calcite (CaCO_3) at elevated pressures reveal⁷³ the appearance of a new band which shows marked pressure dependence of intensity, reversible splitting of one band into two components and of another band into three distinct components, and frequency shifts for two of the bands.

The spectra of benzoic and succinic acids illustrate the effect of pressure on the spectra of hydrogen-bonded substances.⁴⁵ The relatively weak hydrogen bonds are considerably more sensitive to increase in pressure than are normal covalent bonds. Compression of the O...O distances in a hydrogen-bonded structure strengthens the hydrogen bond, and in the case of the organic acids results in a shift to higher frequency for the out-of-plane O—H bending vibration and a shift to lower frequency for the carbonyl str vibration. In general, most large frequency shifts observed for pressures below 50 kbar and most shifts of bands to higher frequencies which persisted above pressures of 10 kbar occurred when hydrogen bonds were present in the structure.

The spectral changes occurring as water⁴⁷ is subjected to increasing pressure and decreasing temperatures yield information on the structures of the dense forms of ice. The frequency shifts and intensity changes observed for the str, bending, and libration modes are consistent with the interpretation that the hydrogen bonds responsible for the open structure of ice I collapse under high pressure to form the close-packed structure of dense ice in which the effect of hydrogen bonding on the vibration modes is only minor.

In ferrocene,⁷³ except for a discontinuous change near 20 kbar indicative of a phase transition, and the appearance of a new band at higher pressure, the pressure-induced changes in the vibrational spectrum are continuous. The vibrational frequencies assigned to the metal-ring and C—C str modes of vibration are the most sensitive to changes in pressure.

Interpretation of Pressure-induced Changes in Infrared Spectra

Interpretation of the pressure-induced changes in the infrared spectra in terms of the structures of the specific substances has usually not been possible. However, a shift to higher frequency may be qualitatively interpreted as the result of an increase in the relative importance of repulsive forces of neighboring molecules. Conversely, a shift to lower frequency indicates that the attractive forces of neighboring molecules are exerting greater influence on the atom or group. Most of the shifts to lower frequency observed to date have been shifts in absorption bands assigned to X—H str vibrations in substances whose structures involve hydrogen bonds. Even for hydrogen bonds, however, there must be some pressure at which the repulsive forces exceed the attractive forces; shifts to higher frequencies should then take place.

Except for hydrogen-bonded substances, an applied pressure of the order of 40 kbar has relatively little effect on the position of most vibrational bands, which indicates that pressures of this magnitude are insufficient to produce significant changes in the modes of vibration responsible for the spectra. Similarly, although the space-group symmetry of the unit cell may be changed by a phase transition occurring at such pressures, the bond configuration is not greatly altered.

At pressures of the order of 40 kbar the decrease in volume for the organic materials studied is approximately 20%.⁴⁵ Since the interatomic distances of atoms involved in the bonds do not change appreciably, the changes in intermolecular distances must be large. The present data indicate that the bonds are relatively insensitive to this change in intermolecular spacing. However, for pressures exceeding 50 kbar, changes in structure occur more frequently. Such a structural change has been observed in *p*-nitrophenol at 160 kbar in studies made with the diamond cell.⁴⁵

For most substances studied⁴⁵ in these laboratories the intensity of the bands decreases with increasing pressure, or remains the same. Occasionally drastic changes occur, such as the apparent disappearance of the absorption band assigned to the nitrite ion bending vibration in NaNO_2 . The interpretation of this marked but reversible change is not yet clear, but the large changes in band intensities which have been observed for several compounds at pressures up to 50 kbar suggest that relatively large changes in dipole moment derivatives are occurring for a number of modes of vibrations.

Pressure in the Diamond Cell, its Nature and Measurement.

The limited amount of information available at present indicates that the pressure exerted on a specimen in the diamond cell is probably not hydrostatic.⁷⁴ Until further evidence is available, the uncertainties concerning the specific nature of the pressure must be kept in mind; meanwhile the stress endured by the specimen will be described by the general term *pressure*.

The absolute value of the pressure endured by the specimen is not known. The applied pressure can be calculated by dividing the applied force by the area of the smaller of the two diamond faces. Frictional forces are neglected. The force is determined by measuring the compression of the spring. When greater precision is required, the thrust transmitted by the specimen may be measured by determining the resistance of a small coil of manganin wire placed between the flange of the bearing and the piston. The calculated applied pressure can be checked by a calibration based on a phase change for a given substance at known hydrostatic pressure and temperature. The transitions of compounds such as NaNO_2 ¹³ and KNO_3 ¹⁴ have been so used.

When the early work on the effect of pressure on infrared spectra was done, little was known about the pressure gradients across the anvil surfaces. In some instances phase transitions occurred over narrow pressure ranges (± 0.3 kbar) with only a single phase present at any time. The sharp transitions were considered evidence that excessive pressure gradients did not exist in the specimen. In other cases more than one phase was present simultaneously over a rather wide pressure range, indicating marked metastability or the presence of a considerable pressure gradient. At first the latter situation was attributed⁷³ to deterioration of the diamonds and use of diamonds of very small area. More recent quantitative work, however, has shown that the pressure gradient across the cell is not negligible.²¹ Indeed, visual observation of materials in the diamond high-pressure cell has provided many striking examples of apparently large pressure gradients across the face of the diamond anvils. The pressure is greatest at the center

of the cell and least at the edges. The gradient can be measured crudely by noting the change in area of a phase transformation with change in anvil pressure. The transition boundary line expands more slowly toward the diamond edge as the pressure increases. This gradient is quite useful as it allows the simultaneous observation by microscopy of several polymorphic phases occurring in the same field of view with the denser phases always occurring toward the cell center. On the other hand, the gradient causes some inconvenience in the study of spectra at elevated pressures. The need to evaluate the pressure gradient and to focus on small areas of the cell in order to obtain accurate spectroscopic measurements led to the development of the microscope spectrophotometer.

THE MICROSCOPE SPECTROPHOTOMETER AND ITS APPLICATIONS

A microscope spectrophotometer (see Figure 14-10) assembled from commercially available instruments has been used²² to obtain visible and near infrared spectra on selected specimen areas as small as $1\mu^2$. Although

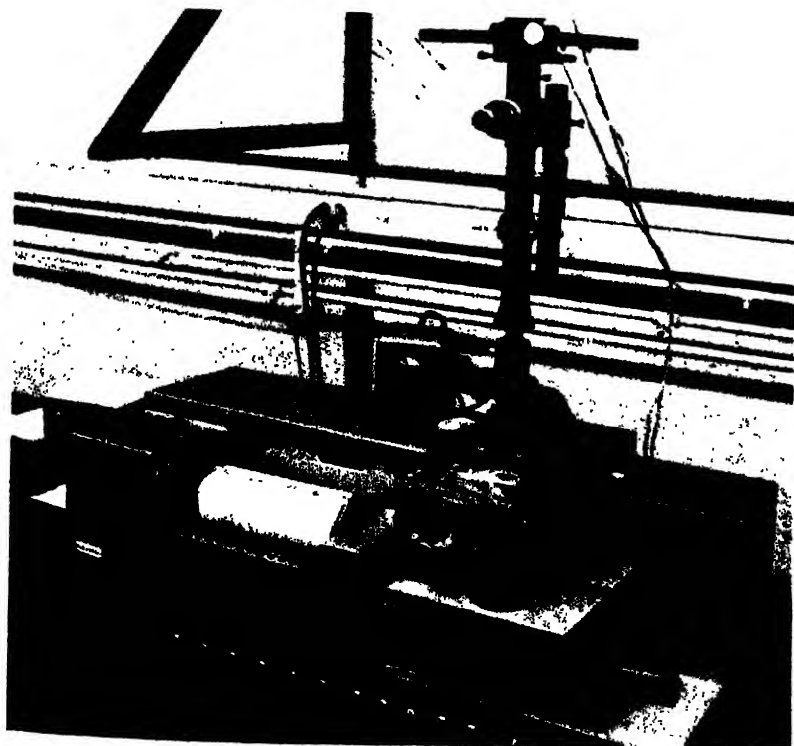


FIGURE 14-10. The microscope spectrophotometer.

originally designed for use in investigating substances in the diamond high-pressure cell, the instrument is equally well suited to the study of conventional microscope specimens.

Components

The principal components are a Perkin-Elmer 350 double beam recording spectrophotometer with a range of 0.2 to 2.7μ and a Leitz ortholux microscope equipped with a phototube to which the photodetector of the spectrophotometer is attached. The microscope spectrophotometer can be assembled easily, quickly, and in a very compact form with a minimum of machine work primarily because of the unusual physical and functional compatibility of the two component instruments. The incorporation of cameras and polarizing optics makes the instrument particularly convenient for phase studies. The instrument has the known characteristics of a proven spectrophotometer and the flexibility and precision as well as visual and photographic accessories of a research microscope.

The details of instrumentation and those performance characteristics altered by the coupling of the two components have been discussed elsewhere.²² Attention will be confined here to applications of the instrument.

Applications

The microscope spectrophotometer has been useful in studying the effect of pressure on the spectra of a number of substances, in determining the pressure gradient in the diamond high-pressure cell, and in obtaining the spectra of microsections of stained biological specimens.

Effect of Pressure on Spectra. The spectra of some substances exhibit pressure-induced shifts in certain absorption bands either to higher or lower frequencies.⁷⁶ If the frequency shift occurs in the visible region, a color change occurs. Nickel dimethylglyoxime, for example, has an absorption band in the visible region which shifts with pressure to longer wavelengths. The thallos halides have an extremely strong absorption band in the ultraviolet region which shifts into and through the visible region as increasing pressure is applied. For some substances the spectral effects of pressure are superimposed on sharp phase transitions. Mercuric iodide, for example, undergoes a transition from the red to yellow form (high pressure), and the absorption edges of both forms are shifted by pressure.

In the diamond high pressure cell the pressure is greatest in the center of the cell and least at the edge. The absorption spectrum of the entire sample under pressure is therefore an average of the spectra at several different pressures; in some cases it is an average of the spectra of different phases as well. Without the microscope spectrophotometer, which can focus on a selected small portion of the cell area, the component spectra

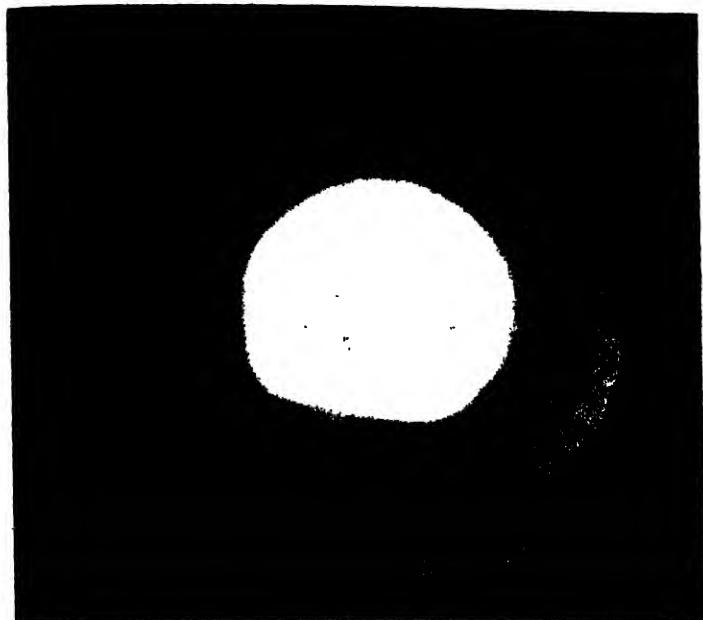


FIGURE 14-11. Photograph of mercuric iodide in diamond cell at an applied pressure of 12 kbar.

cannot be obtained. Figure 14-11 is a photograph of the entire cell area for mercuric iodide at 12 kbar applied pressure. Figure 14-12 gives the spectra obtained with the microscope spectrophotometer of the three forms of mercuric iodide present at this pressure and also the spectrum of the red form at atmospheric pressure.

The complication caused by the pressure gradient across the cell is apparently not as severe for nickel dimethylglyoxime. The location and shift of the absorption band at $19,000\text{ cm}^{-1}$ as a function of pressure obtained from an average spectrum were the same as those reported by Zahner and Drickamer⁴⁰ who studied the compound under a presumably uniform pressure. Nevertheless, the absorption bands are considerably sharper and narrower when measured in a microscope spectrophotometer.

Determination of Pressure Gradient in the Diamond High Pressure Cell. Precise measurement of the magnitude and shape of the pressure distribution in the high-pressure cell is necessary before reliable state and spectroscopic data can be obtained. With the microscope spectrophotometer spectral measurements of selected areas as small as 10^{-7} cm^2 may be made. The area of the diamond surface in the high-pressure cell is 10^{-2} to 10^{-1} cm^2 . Therefore, using a material which has an absorption band whose peak

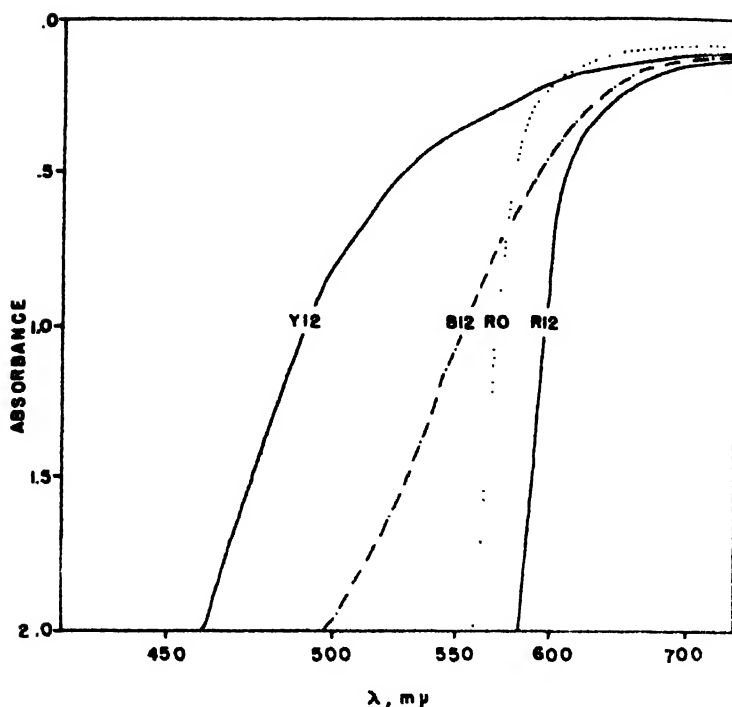
SPECTRA OF HgI_2 IN DIAMOND CELL D-2 AT 0, 12 Kbar

FIGURE 14-12. Spectra of mercuric iodide: at atmospheric pressure, R_0 , the spectrum of the red form at applied pressure of 12 kbar,

R_{12} , the spectrum of red region near phase boundary;

Y_{12} , the spectrum of yellow region near phase boundary;

B_{12} , the spectrum of brownish high pressure region forming at center of sample.

position is known as a function of pressure (such as nickel dimethylglyoxime), one can make as many as 10^4 pressure determinations across the surface of a sample at a given applied pressure.²¹

Alternatively, a photographic technique may be applied to materials which have an absorption edge which shifts with pressure, such as thallium bromide. Successive photographs of the sample in the cell under a given pressure taken with monochromatic radiation of incrementally increased wavelengths may be used to determine pressure contours directly.²¹

The pressure distribution across the diamond surface has been determined by these methods. The pressure P at a distance r from the center of the cell may, as a first approximation, be expressed by the equation²¹

$$P = P_m \left[1 - \left(\frac{r}{r_o} \right)^2 \right] \quad (14-1)$$

where r_o is the radius of the anvil surface and P_m is the pressure at the center of the cell.

In the investigation using nickel dimethylglyoxime, in which an alkali halide diluent was used to improve the quality of the spectroscopic data, the pressure was found to depend on diluent concentration and also on

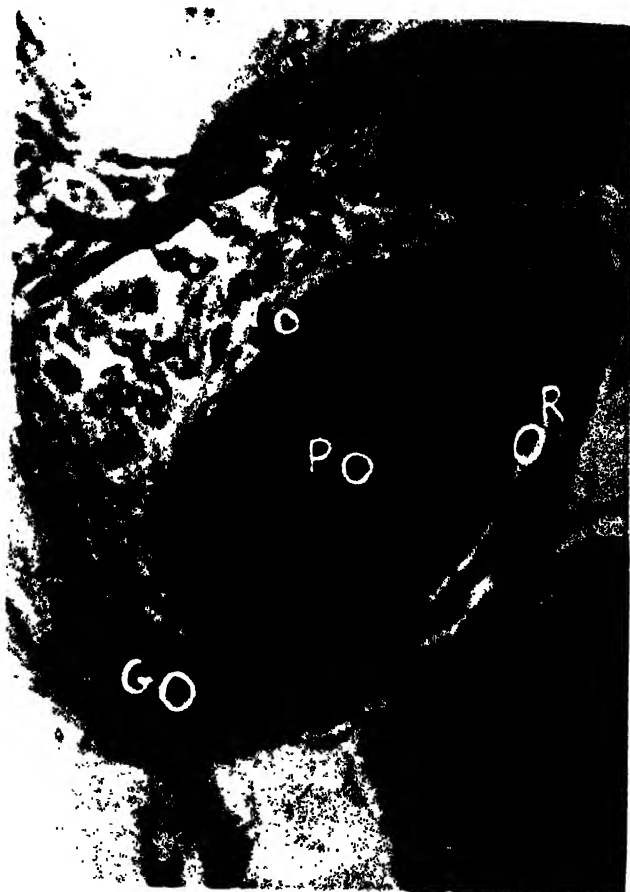


FIGURE 14-13. Photograph of stained thin section of sheep hair follicle.

the particular diluent used. The pressure gradient decreases with increasing concentration and compressibility of the diluent. From a consideration of the mathematical relationships for substances under pressure between fixed non-deformable anvils, an expression for the pressure gradient in terms of the compressibility of the material has been derived. For the compounds studied, the calculated values agree well with those obtained experimentally.

Spectra of Microsections of Stained Biological Specimens. The application of the microscope spectrophotometer to conventional microscope specimens may be demonstrated²¹ with a thin section of a sheep hair follicle stained with safranin and fast green dyes. Figure 14-13 is a photograph of the specimen with the colors of the various areas indicated by letters. The green area is connective tissue, the deep purple area is follicle tissue, the red area consists of sebaceous cells surrounding the hair follicle, and the reddish purple area consists of nuclei of the tissue cells. The spectra of the small sections circled in the photograph are shown in Figure 14-14. For all except one of these sections $10\mu^2$ scan areas were used. For the determination of the spectrum of the nuclei of the tissue cells, the scan area was $1\mu^2$. A 100X achromatic objective was used in obtaining these spectra.

Advantages

The microscope spectrophotometer described here, when equipped with the proper optics, should be useful wherever microanalytical spectroscopic techniques are required. The instrument is particularly valuable when only small quantities of material (as small as 10^{-9} g) are available or when the sample is nonhomogeneous. In addition, it can be used for ultraviolet, visible, and near infrared spectral determinations on samples which require working distances up to 15 mm. The instrument is adaptable to spectral observations of materials under pressure or in a vacuum, and at cryogenic or elevated temperatures.

SOME ADDITIONAL APPLICATIONS OF THE DIAMOND CELL

The diamond cell has found many additional uses⁷⁶ since its development in 1958.^{74,75} It has been used to investigate the nature and optical characteristics of polymorphic changes in transparent liquids and solids and has provided easy access to regions of phase diagrams otherwise observable only with more elaborate apparatus and considerably more tedious techniques. Crystal growth phenomena can also be observed. The cell can be used to study the fluorescence and phosphorescence, and visible and ultraviolet spectra of samples either at atmospheric or elevated pressures over a wide range of temperatures. X-ray crystallographic data for several

SPECTRA TAKEN FROM SELECTED AREAS OF SHEEP HAIR FOLLICLE (X.S.)

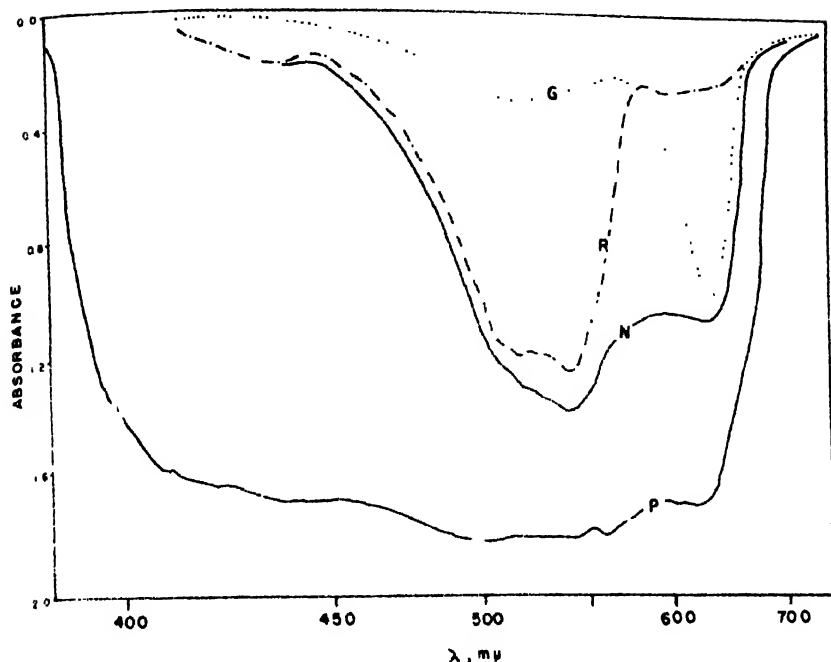


FIGURE 14-14 Spectra of selected areas circled in Figure 14-13:

G denotes the green area which is connective tissue.

R denotes the red area which is sebaceous cells surrounding hair follicles;

P denotes the deep purple area which is the follicle tissue.

N denotes the reddish purple area which is the nuclei of the tissue cells.

salts and metals have been obtained using the diamond cell. In some cases new high-pressure phases were detected.

The wide range of problems in which the cell is applicable, its miniature size, and the relative simplicity of the experimental techniques involved in its use, make the development of the diamond cell a marked advance in applied spectroscopy and high-pressure technology.

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CHAPTER

15

Attenuated Total Reflectance

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INTRODUCTION

The development of the Attenuated Total Reflectance (ATR) technique since its introduction in 1959 by Fahrenfort¹ has proceeded in three principal directions: analytical applications, the determination of optical constants, and the development of instrumentation for exploiting the technique. Devising appropriate instrumentation has been concurrent with the other two directions.

This chapter is concerned primarily with the analytical applications of the ATR technique. Using this technique, however, index of refraction, n , and extinction coefficient, κ , can be determined more accurately and quickly than by ordinary reflection procedures. Refractive index n' is in general a complex number and can be written

$$n' = n - i n \kappa \quad (15-1)$$

The real part, n , is the ratio of the velocity of light in the two media adjacent to the reflecting interface. The imaginary part $n\kappa$, the product of the two optical constants, is related to the damping of the amplitude of the light wave in the second medium, and is linked to the absorption coefficient α of Lambert's Law by

$$\alpha = \frac{4\pi n \kappa}{\lambda} \quad (15-2)$$

*Barnes Engineering Co., Stamford, Connecticut.

Thus the determination of the optical constants n and κ from reflection is equivalent to the determination of absorption coefficient from transmission. The reader is referred to Refs. 2 and 3 for the theory and practical details of the methods for determining optical constants from reflection spectra.

Essentially the instrumentation for producing ATR spectra is currently in a state of flux. While special commercial instruments are available for scanning ATR spectra, this technique is presently carried out mainly by means of an accessory mounted in a normal infrared spectrometer.

Analytical applications represent by far the largest effort which has gone into the development of the ATR technique. It has found particular usefulness and acceptance in the analysis of plastics, resins, and coatings of various kinds.

THE ESSENCE OF ATR

The ATR technique is a type of internal reflection spectroscopy and should be differentiated from other forms of reflection spectroscopy.

Specular reflectance is that in which radiation strikes the front surface of a sample and is reflected back into the monochromator by a mirror or set of mirrors. Specular reflectance devices may use either a fixed or changeable angle. A pure specular reflectance spectrum does not resemble a transmission spectrum.

Another commonly practiced form of reflectance spectroscopy is that in which a thin film is coated on a highly reflecting surface, such as aluminum, and the whole is inserted into a specular reflectance accessory. The resulting spectrum does resemble a conventional transmission curve. This type of reflection spectroscopy is sometimes referred to as 2X transmission, because the radiation passes through the sample, strikes the reflecting surface, is directed through the sample again, and then enters the monochromator. The 2X transmission technique is widely used but limited to very thin samples. It works best with clear, unfilled samples which are at least moderately good film formers. It breaks down almost completely when samples are too thick or opaque.

Radiation is propagated through a crystal by total internal reflection. So long as the reflection remains total, no spectrum will be produced. An ATR spectrum is produced only after one has met the conditions for attenuated total reflectance: in one or more locations along the crystal, where the reflection would otherwise be total, a sample is introduced of refractive index lower than that of the crystal at an angle above the critical angle. The critical angle is that angle of incidence for which the angle of refraction is 90° .

The angle of incidence required for critical reflection is given by Snell's law

$$n_p \sin \theta = n_s \sin \phi \quad (15-3)$$

where n_p and n_s are the refractive indices of the ATR crystal and the sample, respectively; θ is the angle of incidence and ϕ is the angle of reflection. At the critical angle $\phi = 90^\circ$, hence $\sin \phi = 1$. The angle of incidence required for critical reflection then becomes, substituting in Equation 15-3,

$$\sin \theta = \frac{n_s}{n_p} \quad (15-4)$$

Four crystal materials have been found to be the most useful as ATR crystals. These are, in decreasing order of utility: thallous bromide-iodide, silver chloride, "Irtran-2," and germanium. KRS-5 is by far the most widely used crystal.

Thallous bromide-iodide (KRS-5), with its refractive index of 2.38, generally requires an angle of incidence about 40° whenever the refractive index of the sample is near 1.5. Silver chloride, with a refractive index about 2.0, requires an angle of incidence of 50° or more for the same sample refractive index. "Irtran-2," with its 2.25 refractive index, requires angles of incidence just above 40° ; germanium, with $n = 4.02$, needs about a 20° angle of incidence for critical reflection.

Table 15-1 below shows the relationship between the refractive index of the most widely used ATR crystal materials and a range of refractive indices of organic compounds.

TABLE 15-1. ANGLES FOR CRITICAL REFLECTION

Material	Crystal Refractive Index	Incident Angles ($^\circ$) Refractive Index of Sample			
		1.3	1.4	1.5	1.6
KRS-5	2.38	33	36	39	42
AgCl	2.0	40	45	49	53
"Irtran-2"	2.25	35	38	42	45
Ge	4.02	19	20	22	24

The fundamental requirement for producing a useful ATR spectrum is that the infrared radiation enter a crystal of high refractive index, strike a sample of lower refractive index one or more times at an angle above the critical angle at the reflecting interface, and exit through the crystal into the monochromator. The resulting spectrum is very similar to the conventional spectrum obtained by transmission techniques in the infrared region.

As wavelength increases, the apparent absorption bands in an ATR spectrum tend to appear deeper than the corresponding bands in a transmission spectrum. This is the most noticeable difference between ATR and transmission and originates with the wavelength dependence of ATR. Another difference, rarely observed, is a small shift in the apparent absorption maxima. Neither difference seriously impairs the comparison of ATR with transmission spectra.

When the angle of incidence approaches the critical angle only fair or poor spectra are obtained because of the distorting effects of refraction.⁶ Nevertheless, the intensity of the absorption bands decreases as the interval from the critical angle increases. Moreover, as the refractive index of the crystal approaches that of the sample, the ATR spectra become more intense. The absorbance of the bands in the spectrum becomes greater. A compromise is required to obtain the optimum ATR spectrum. The selection of the crystal to use is more important than the range of angles of incidence at which it is to be used. The spectroscopist then optimizes the incident angle, always greater than that required for critical reflection, but not so great as to produce a weak spectrum, nor so small as to yield a refraction-distorted spectrum. This optimization procedure will be discussed further under "Sample Preparation."

ATR INSTRUMENTATION

The developments in ATR instrumentation have been largely in the selection and evaluation of crystals of different configurations. The configurations of the crystals are intended to provide reflections ranging in number from one in simple prisms or hemi-cylinders, to as many as twenty or more using larger-than-single or double-pass crystal slabs.⁵

Most ATR work is done by means of an accessory readily inserted in, and readily removed from, a conventional infrared spectrometer or spectrophotometer. The accessory consists of a mirror system which sends the source radiation through a crystal at an adjustable or fixed angle of incidence, and a second mirror system which directs the radiation into the monochromator of the infrared instrument. The ATR crystal or elements holder is normally designed so that samples can be brought into contact with the crystal surface and some form of pressure exerted to produce the required intimate contact between sample and crystal. Similar mirror arrangements provide for fixed angle work which is of growing importance.

This accessory is mounted in the sampling space of the spectrophotometer. ATR accessories permanently mounted in an infrared instrument are also commercially available.

The average transmittance through a single piece of KRS-5 no thinner than 2 mm is about 55% at an angle of incidence between 45 and 55°. Transmittance goes down to about 10 to 12% when germanium is used. Normally the reference beam is attenuated to compensate for the energy loss, i.e., to spread out the spectrum to full scale. It is completely unnecessary to widen the slits.

SAMPLE TECHNIQUES

Production of a satisfactory ATR spectrum requires the judicious selection of the appropriate ratio between the refractive index of the crystal and that of the sample, of the angle of incidence which the radiation makes at the crystal-sample interface, and the contact between the sample and the crystal. The contact which the sample is able to make with the ATR crystal is vital. Without adequate contact, no useful spectrum will ever result.

The best ATR spectra are those which have been obtained using smooth samples. Smooth samples, such as films, result in an intimate contact between the sample and crystal and produce little, if any, damage to the polished surface of the crystal, thereby extending its useful life.

If a sample possesses a rough surface, no amount of digging it into the back of a prism, even using extreme pressure, will help. The infrared beam simply gets lost, no spectrum will result and the ATR prism will either be ruined, or at best require repolishing. It is also not sufficient that the sample simply contact the ATR crystal surface at some points and not at others. Again the beam gets lost and no spectrum results. If the sample surface can not be made smooth without destroying that of which the spectroscopist wants to take a spectrum, then ATR is not the technique to choose.

To obtain a satisfactory spectrum of a coating on a substrate, the coating must have a thickness detectable by infrared. This means at least about 0.001 mm thickness.

ATR spectra can be scanned on powders if they are cohesive. Examples are relatively few. Among them are butyl rubber, finely ground melamine-formaldehyde, and melamine-urea resins. There is a better chance of obtaining a satisfactory spectrum from a fine powder than a coarse one. If a powder can be prepressed to the required shapes, this improves the chances of securing a spectrum. The ATR crystal holder is not designed to serve as a press and will not work as one. Fine polyethylene powder, if pressed in the holder, does not yield a spectrum, but if prepressed in a die, the curve resulting is excellent.

Radiation penetrations into solutions of the order of 0.005 to 0.05 mm are possible. If a solution component will give a spectrum within this path-

length range, then it can be developed. For an aqueous solution the spectrum will be that of water to the extent that penetration has been effected; a 0.05 mm penetration means a nearly complete blackout of the spectrum.

The selection of the ATR crystal for any given sample can begin with the finding that to date KRS-5 has been perhaps a hundred times more useful than AgCl. In general, all colored materials, films, and paints should be tried using a KRS-5 crystal. Polystyrene is an exception for which a AgCl crystal works best. When finding the optimum angle of incidence for a particular sample with a KRS-5 crystal, an angle of 45° is a good starting point. In general, do not seek maximum energy output; it does not necessarily give maximum sample penetration. TiO_2 is an exception. If one has reason to believe a paint panel, e.g., contains TiO_2 , seek out maximum energy at 2000 cm^{-1} (5μ). Such usually obtains at about 55° .

AgCl as an ATR crystal works well for clear films, some colored films, and for samples containing polystyrene. A good incidence angle starting point when using AgCl is 60 to 55° . The AgCl crystal has a more limited range than KRS-5, and outside this range shows more severe spectral distortion. Distortion of a spectrum is readily recognized and occurs on the long-wavelength side of a band. A rubber sample known to be high in sulfur content should not be used on AgCl because of silver sulfide formation.

"Irtan-2," because of its insolubility, is especially useful for water solution studies. It is also of interest that the transmission limit of "Irtan-2" (about 11μ) coincides with the region where total absorption of water begins. Use of an "Irtan-2" ATR crystal will usually show no spectral distortion when employed at angles of incidence between 65 and 75° .

Germanium is an ATR crystal suited to multiple reflection techniques. Weak spectra result when it is used in a single ATR pass except with samples of low refractive index, about 1.3, such as silicone rubber which gives a moderately intense ATR spectrum even in a single pass.

Chemical reactions between ATR crystals and samples should be avoided. They will destroy the crystal as well as the ATR effect. This is another reason why special purpose crystals should be available. An "Irtan-2" crystal, e.g., can be used to study the ATR spectra of polymers dissolved in aqueous thiocyanate solutions. Both KRS-5 and AgCl crystals react with thiocyanate.

It is important to be able to determine where refraction distortion in an ATR spectrum begins, particularly if one wishes to identify an unknown based on a comparison against a conventional transmission spectrum. Probably a graphical procedure is best. Plots of apparent absorbance versus angle of incidence at a specific frequency are made. Refraction distortion begins where the slope of the curve changes. Without such a graph it is

difficult to predict the exact point at which the change in slope will occur because in a region of heavy absorption the refractive index is changing rapidly.

The term "apparent absorbance" was used above because bands in the spectrum of a given sample show an increase in apparent absorbance with decreasing refractive indices of the ATR crystal employed. A spectrum of polystyrene film obtained with a AgCl crystal at 60° incidence yields bands of greater absorbance than a spectrum of the same film obtained with a KRS-6 crystal at 50° incidence. KRS-6, thallous chloride-iodide, has a refractive index of 2.19 in contrast to that of 2.0 for AgCl.

APPLICATIONS

The ATR technique, as previously discussed, yields infrared spectra that are comparable to those obtained by the transmission technique if proper consideration is given to the choice of a crystal material. The ATR crystal should be selected primarily on the basis of the refractive index of the sample. The ratio between the refractive indices of the sample and the crystal will define a range of incident angles within which spectra can be obtained. Outside of this range, spectra will either be weak or show the distorting effects of refraction.

The differences between specular reflectance, the "2X transmission" type of reflectance, true transmission, and an ATR spectrum are shown in the following spectra of polystyrene. Figure 15-1 illustrates specular reflectance. A thin film was used, the sample was unbacked, and the angle of incidence was 90° . Note that the spectrum consists predominantly of fringes with very few bands which approximate absorption bands in evidence. Figure 15-2 shows the spectrum of the same 0.07 mm thick film.

For this curve, a specular reflectance unit with a 90° incidence angle was used, and the film was backed with polished aluminum. This spectrum illustrates "2X transmission" reflectance. It is slightly more than twice the intensity of a transmission spectrum of the same film. Figure 15-3A shows a conventional transmission spectrum of the identical polystyrene film. The ATR spectrum of this film, Figure 15-3B, employing a 2 mm KRS-5 crystal shows the wavelength dependence of the ATR technique. The bands at longer wavelengths get deeper and appear to be stronger than they are in the transmission spectrum.

In Figure 15-4 the ATR spectrum of plasticized polyvinyl chloride is seen. Three reflections were made at a 45° angle of incidence with a KRS-5 crystal. Note that none of the absorption bands characteristic of polyvinyl chloride are observed. The spectrum is entirely that of the plasticizer. Here then is a convenient easy procedure for obtaining the spectrum of plasti-

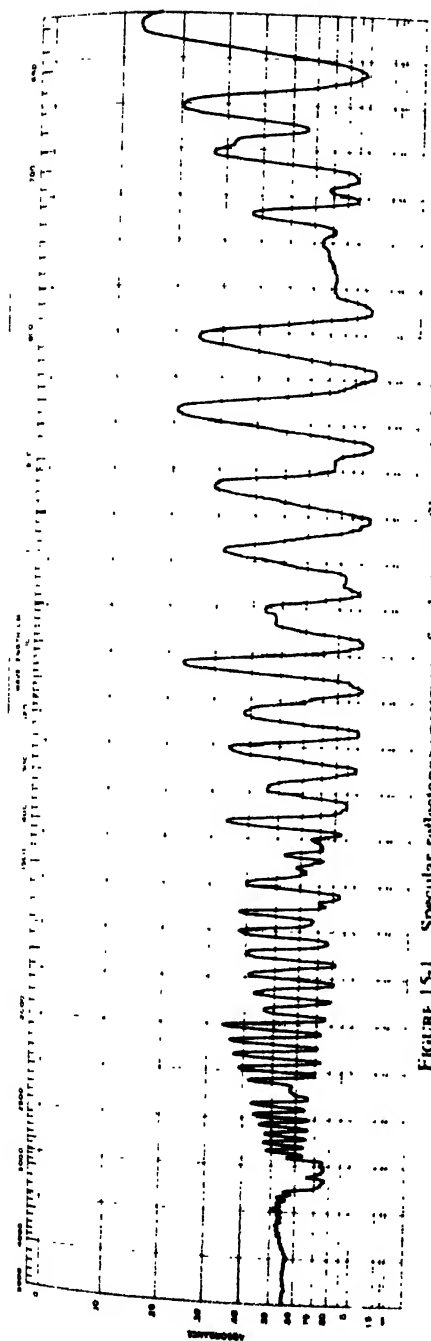


FIGURE 15-1. Specular reflectance spectrum of polystyrene film, unbacked, 90° incidence.

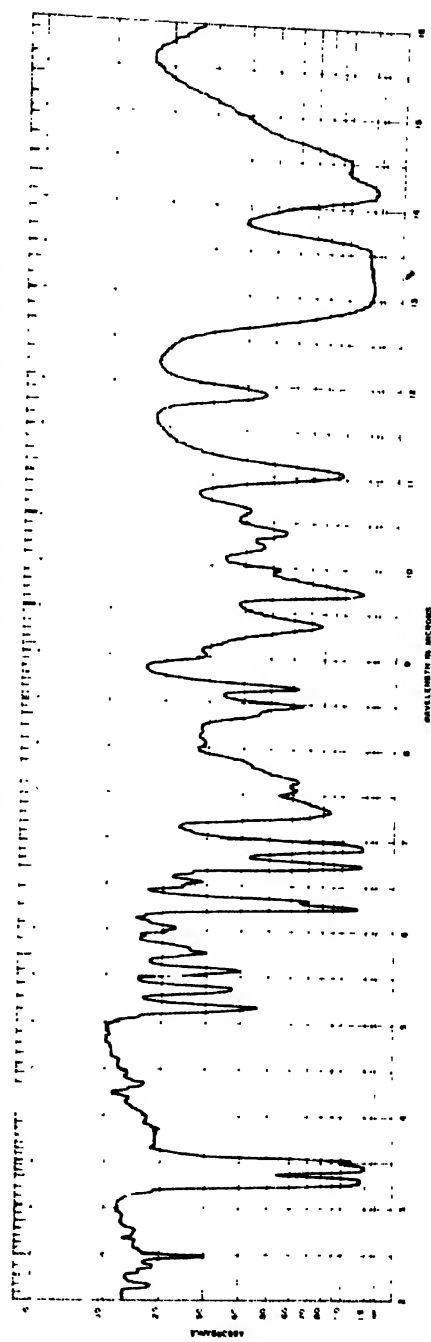


FIGURE 15-2. Specular reflectance spectrum of polystyrene film, polished aluminum backing, 90° incidence.

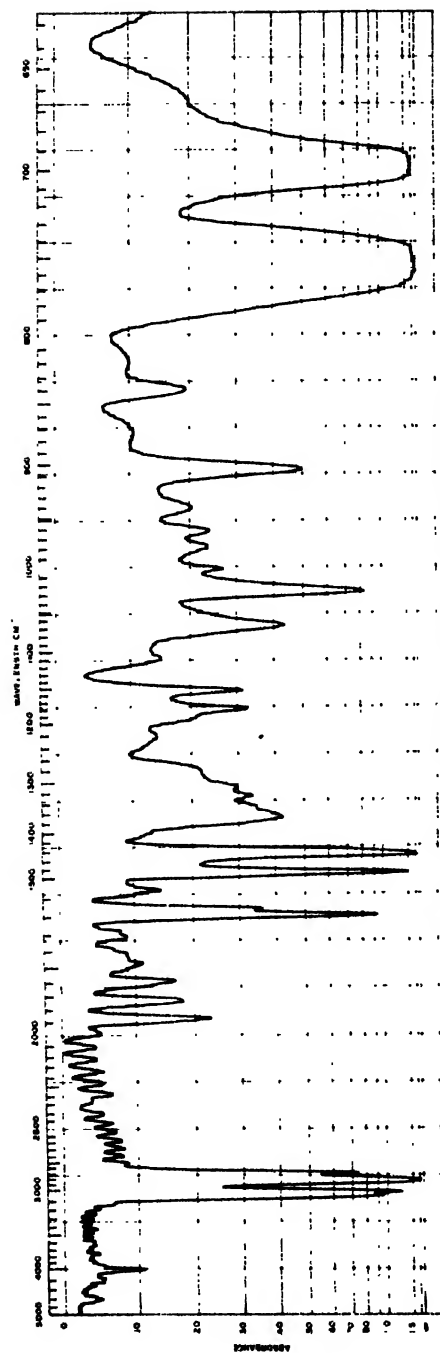
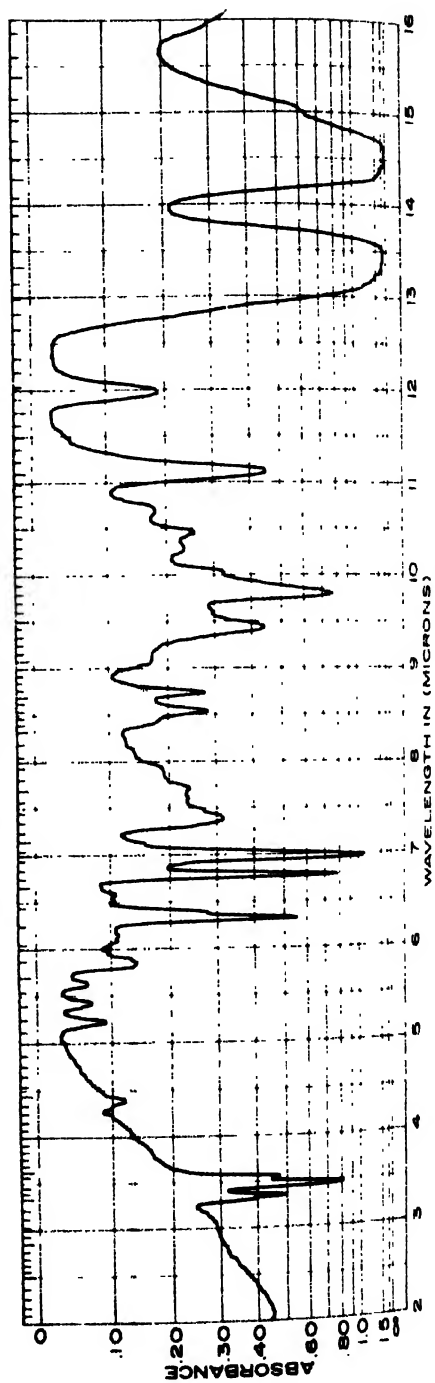


FIGURE 15-3A. Transmission spectrum of polystyrene film.



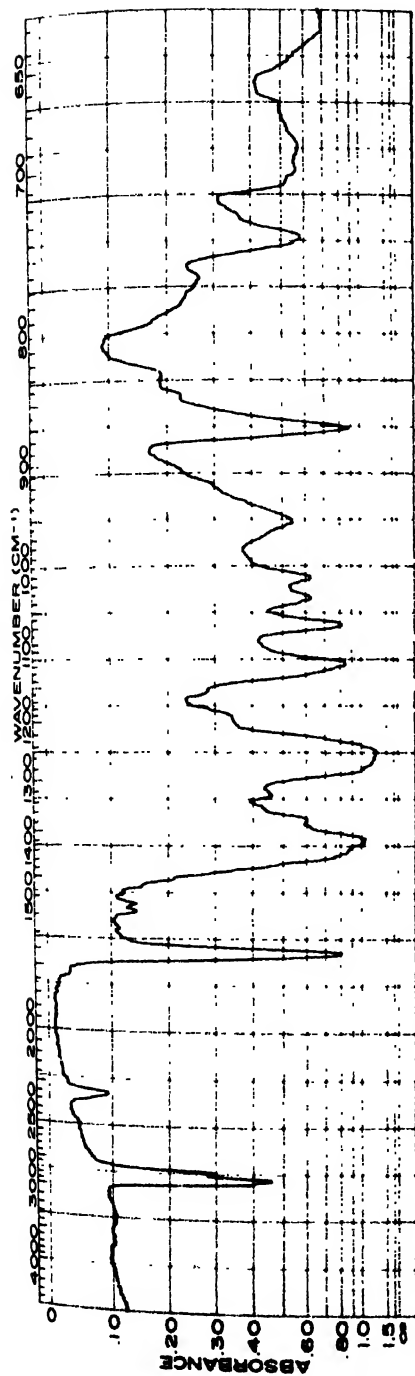


FIGURE 15-4. ATR spectrum of plasticized polyvinyl chloride, 45° incidence, KRS-5 crystal, three reflections.

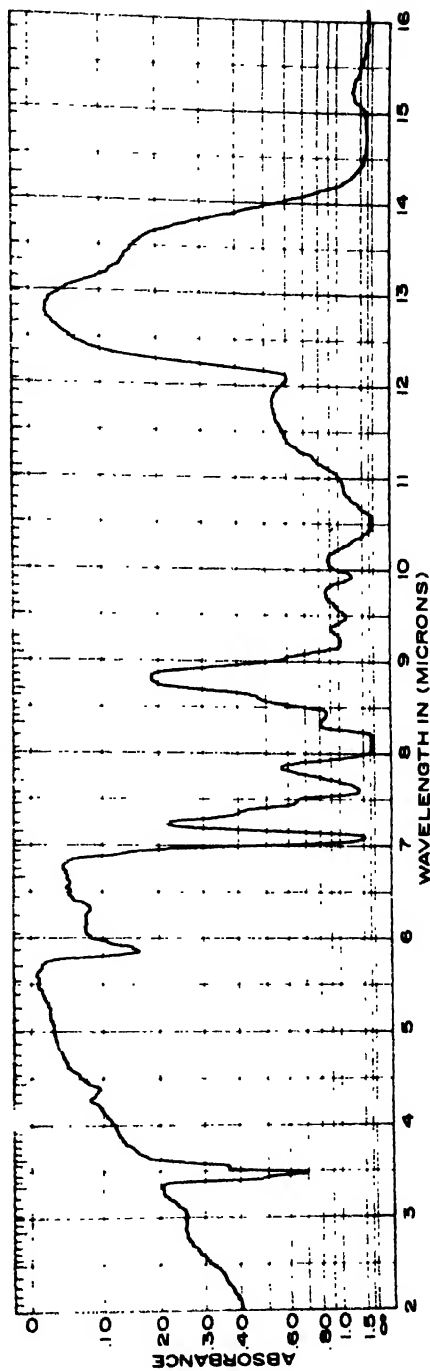


FIGURE 15-5. ATR spectrum of unplasticized polyvinyl chloride, KRS-5.

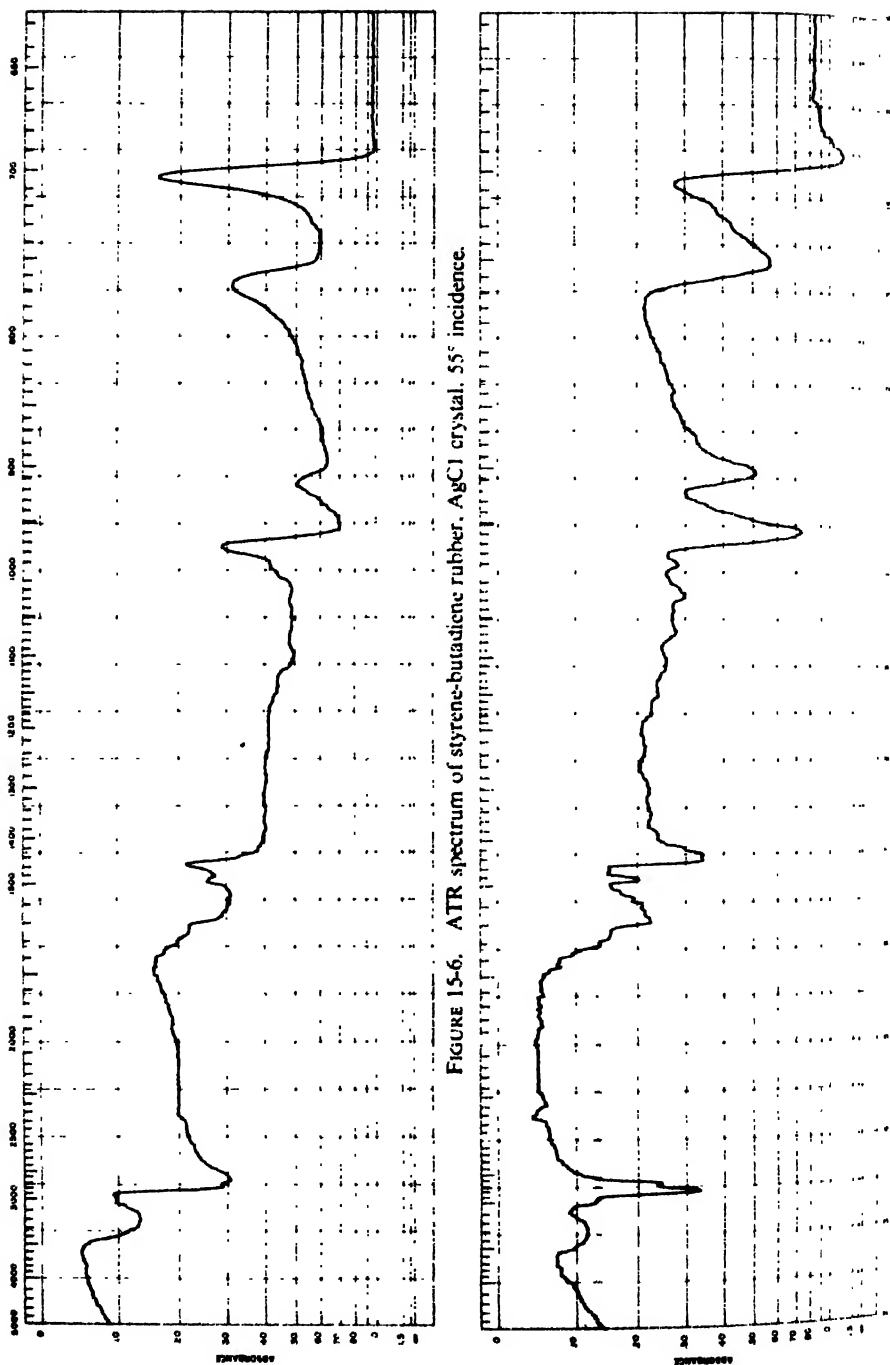


FIGURE 15-6. ATR spectrum of styrene-butadiene rubber. AgCl crystal, 55° incidence.

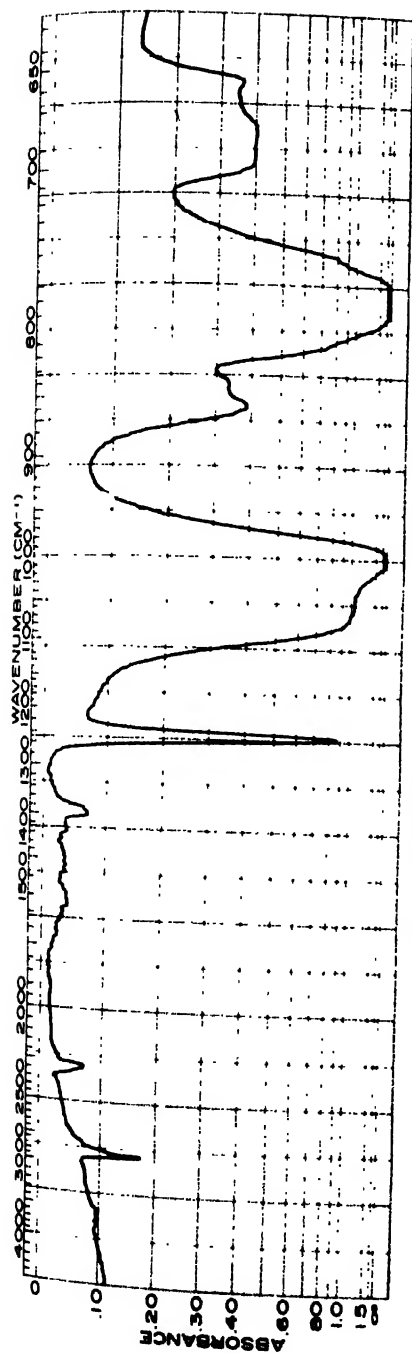


FIGURE 15-8. ATR spectrum of silicone rubber, KRS-5 crystal, one reflection.

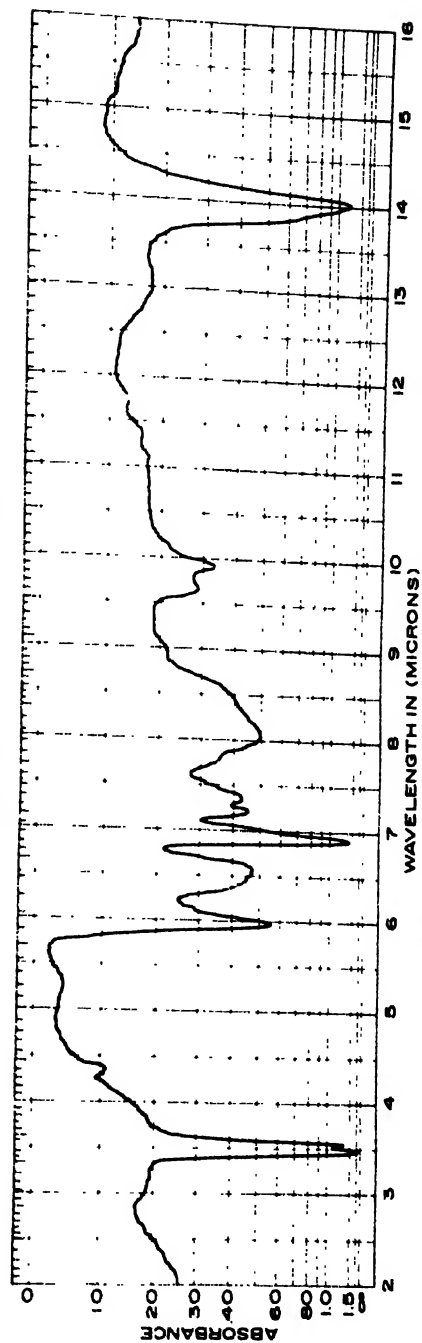


FIGURE 15-9. ATR spectrum of duPont "Surlyn", KRS-5 crystal.

cizers uncomplicated by absorptions of the polymer. Figure 15-5 shows an ATR spectrum, using a KRS-5 crystal, of unplasticized polyvinyl chloride

The effect of proximity to the critical angle is shown in Figure 15-6. This ATR spectrum of a styrene-butadiene rubber resulted from use of an AgCl crystal at a 55° angle of incidence. Observe that the absorption bands appear upside-down in the region between 1450 to about 700 cm^{-1} (6.89 to 14.3μ). The inverted peaks have moved to higher frequencies as evidenced by comparison with Figure 15-7. This ATR spectrum of the same styrene-butadiene rubber resulted from use of an AgCl crystal at a 62.5° angle of incidence. Note that the bands are distorted only from about 750 to 650 cm^{-1} .

Silicone rubber is one of the easiest samples to use for ATR work. Figure 15-8 results from a single reflection employing a KRS-5 crystal. The great intensity arises because linkages involving silicon atoms yield bands about five times more intense than bands from corresponding carbon linkages, as first explained by Wright and Hunter.⁷

Spectroscopists are sometimes confronted with polymers very difficult or impossible to dissolve. In such cases, preparation of an appropriate thickness film for transmission work by the cast film sampling procedure is not possible. An ATR spectrum, on the other hand, may be fairly easy to obtain. "Surlyn," a charged ionic polyethylene of duPont manufacture, is such a polymer. Figure 15-9 shows an ATR spectrum of "Surlyn" employing a KRS-5 crystal.

Acrylonitrile-butadiene-styrene (ABS) is a synthetic polymer frequently used in the fabrication of luggage. The knobby texture of its surface makes it difficult to use in ATR work unless pressure is carefully applied. Figure 15-10 shows the ATR spectrum of "Boltaron," an ABS, obtained with a 2 mm KRS-5 crystal.

Films of polyvinylidene fluoride too thick for conventional transmission work are frequently encountered. Such are no problem for ATR. Figure 15-11 shows an ATR spectrum of polyvinylidene fluoride obtained using a 2 mm KRS-5 crystal.

The effect of varying the number of reflections using a multireflection ATR crystal is illustrated below with cellulose propionate as the sample. Figure 15-12A shows the ATR spectrum obtained from 20 reflections with a 2 mm KRS-5 crystal; Figure 15-12B, that obtained from 10 reflections using the same crystal. The observed intensities between the spectrum from a small number of reflections and a large number of reflections is rarely proportional. Increasing the number of reflections does not increase the intensity of the spectrum correspondingly. At present there is very little angle of incidence control when a large number of reflections is used. It is possible, however, to control the angle of incidence when a small number of reflections is involved.

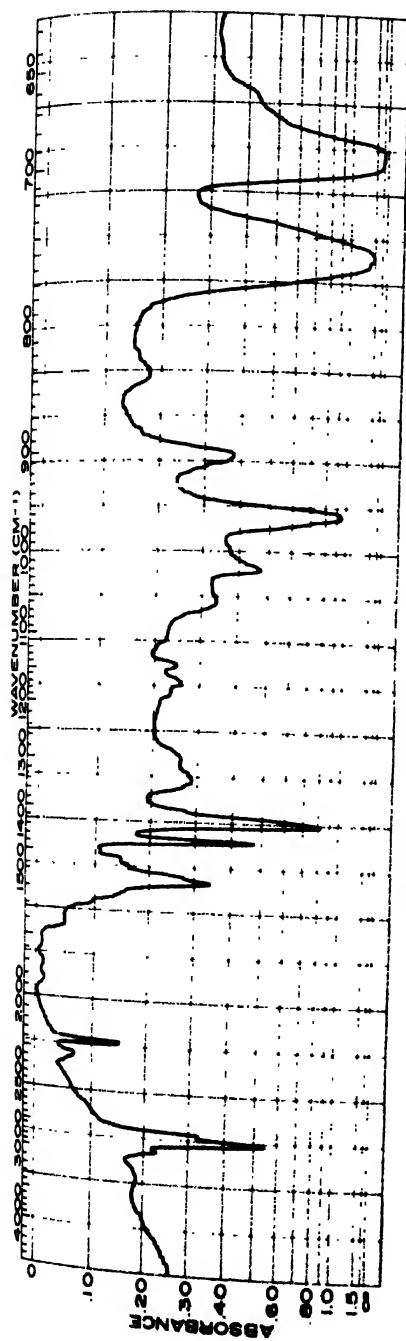


FIGURE 15-10. ATR spectrum of "Boltaron", KRS-5 crystal.

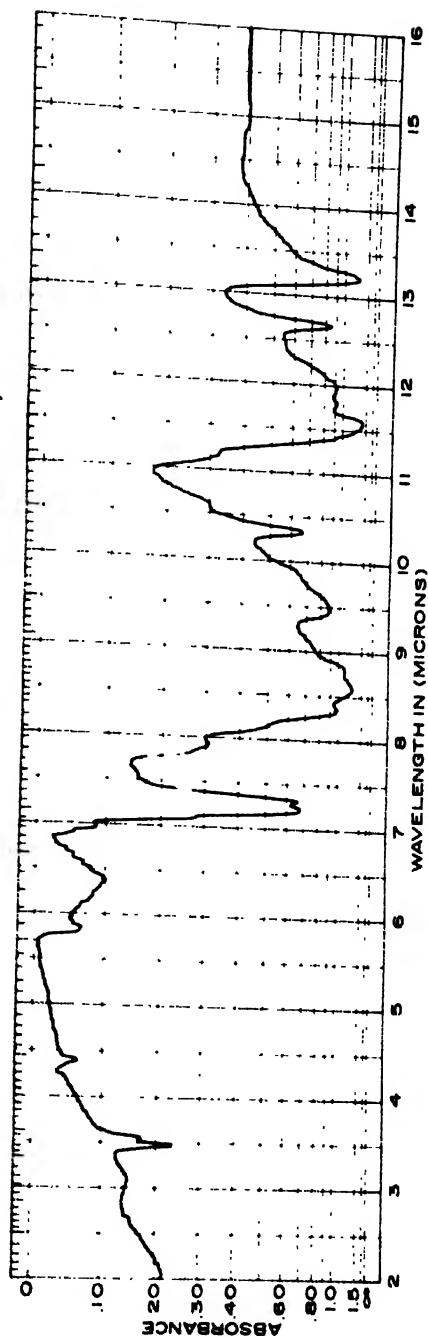


FIGURE 15-11. ATR spectrum of polyvinylidene fluoride, KRS-5 crystal.

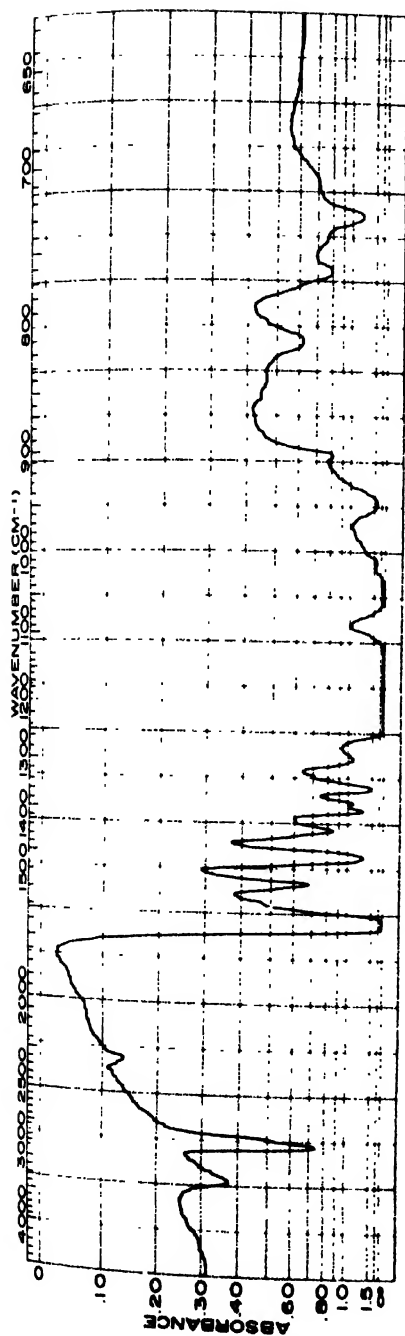


FIGURE 15-13A. ATR spectrum of a polyurethane elastomer, KRS-5 crystal.

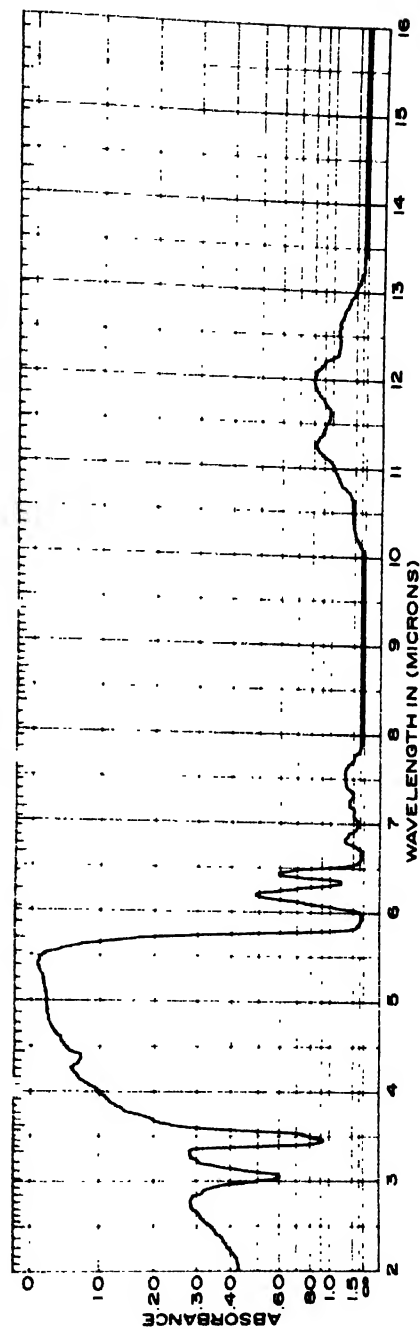


FIGURE 15-13B. ATR spectrum of a synthetic leather, KRS-5 crystal, 20 reflections.

Figure 15-13A shows the ATR spectrum of a polyurethane elastomer obtained with a 2 mm KRS-5 crystal. The spectrum of a synthetic leather based on polyurethane is shown in Figure 15-13B. The curve is much too strong when 20 reflections are used. When only 10 reflections are used, Figure 15-13C, the spectrum is more definitive.

An ATR spectrum was scanned on a coated paper for the purpose of identifying the binder. Figure 15-14A shows the curve obtained when 20 reflections were used. This curve illustrates how strong an ATR spectrum can be. Figure 15-14B shows the curve obtained when 10 reflections were used. The spectrum of the china clay in the coating is observed. The coating binder was not observed because its concentration is below the detectability threshold of the ATR technique.

When polyethylene is coated on aluminum by an open flame melting or softening process, the ATR technique can be used to measure the carbonyl formation. The carbonyl band near 5.9μ is readily observed in Figure 15-15, the spectrum of such a coating using KRS-5 and five reflections. The change to an unresolved doublet near 14μ from the resolved doublet of conventional polyethylene is very obvious. Other spectral differences will be observed if one compares this spectrum against that of the usual polyethylene film.

One of the more common uses of ATR is to identify the components of a two-sided laminated film. Figure 15-16A shows the ATR spectrum of one side of the film; Figure 15-16B, that of the other side of the film. Side A is "Mylar" and side B is a polycarbonate. Evidently polycarbonate was coated onto "Mylar" to form this laminate.

Nitrocellulose is often encountered in ATR work. Figures 15-17A and 15-17B represent multireflection ATR spectra of two nitrocellulose coatings on cellophane. The samples were the cellophane wrappers from two different brands of cigarettes. Characteristic nitrocellulose absorptions are evident in each spectrum but nitrocellulose is obviously not the only component observed. Furthermore, only a casual comparison shows there are differences in the chemical components present as between the two wrappers.

THE FUTURE OF ATR

The ATR technique is developing rather rapidly along several fronts. New crystal materials and novel designs of accepted crystals are constantly being explored. The design of new multireflection accessories can be expected. The ATR effect is being explored in the ultraviolet and visual regions of the electromagnetic spectrum⁴ as well as in the infrared.

The technique of obtaining satisfactory ATR spectra from an ever widening variety of samples is progressing. In the early days of ATR satisfactory spectra just couldn't be obtained from some samples. Ingenuity

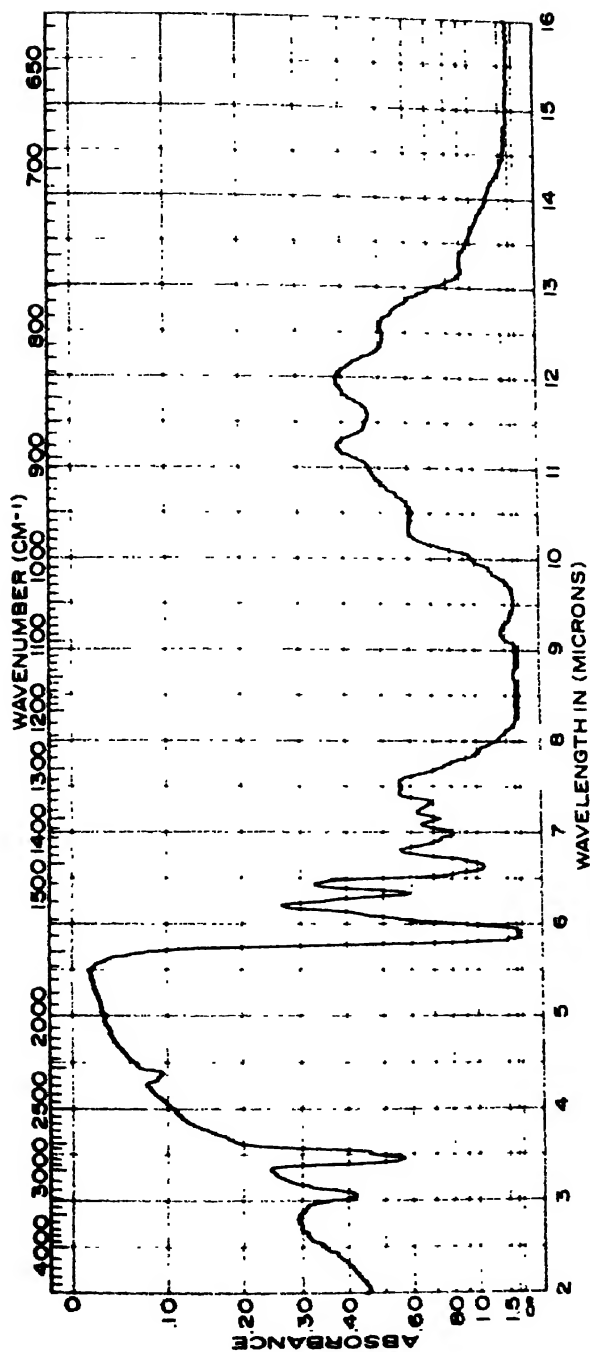


FIGURE 15-13C. ATR spectrum of a synthetic leather, KRS-5 crystal, 10 reflections.

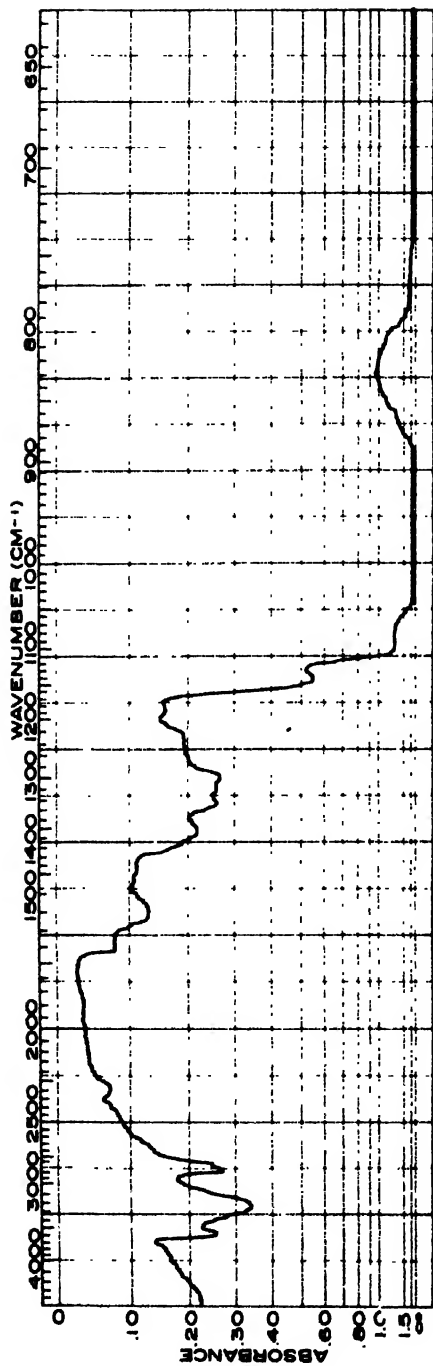


FIGURE 15-14A. ATR spectrum of coated paper, KRS-5 crystal, 20 reflections.

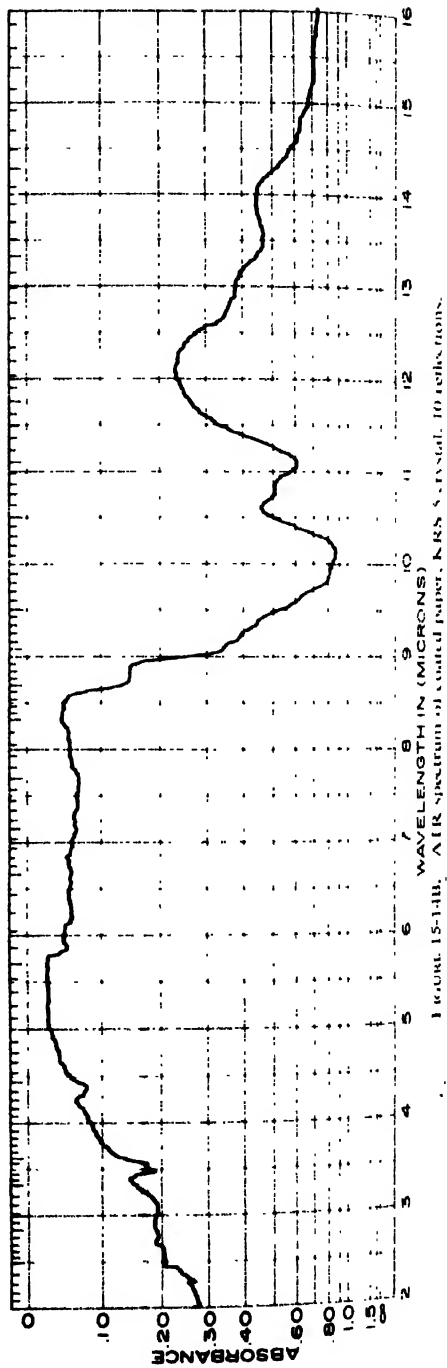


FIGURE 15-14B. ATR spectrum of coated paper, KRS-5 crystal, 10 reflections.

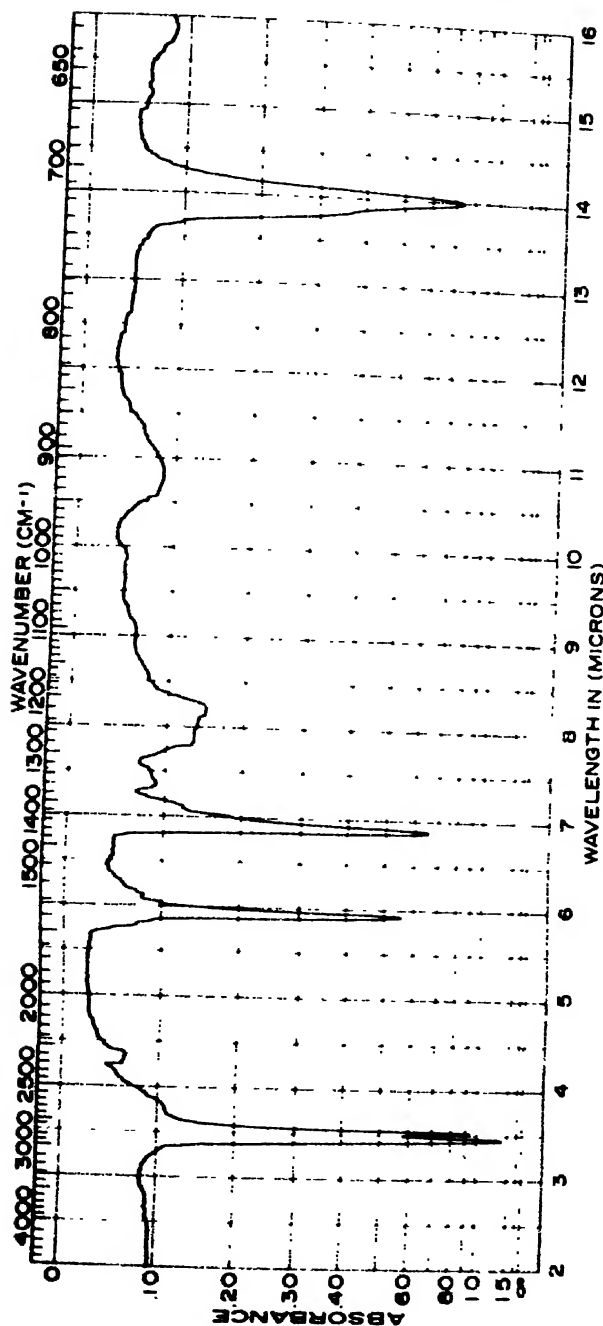


FIGURE 15-1: ATR spectrum of polyethylene coated on aluminum by open flame melting, KRS-5 crystal, 5 reflections.

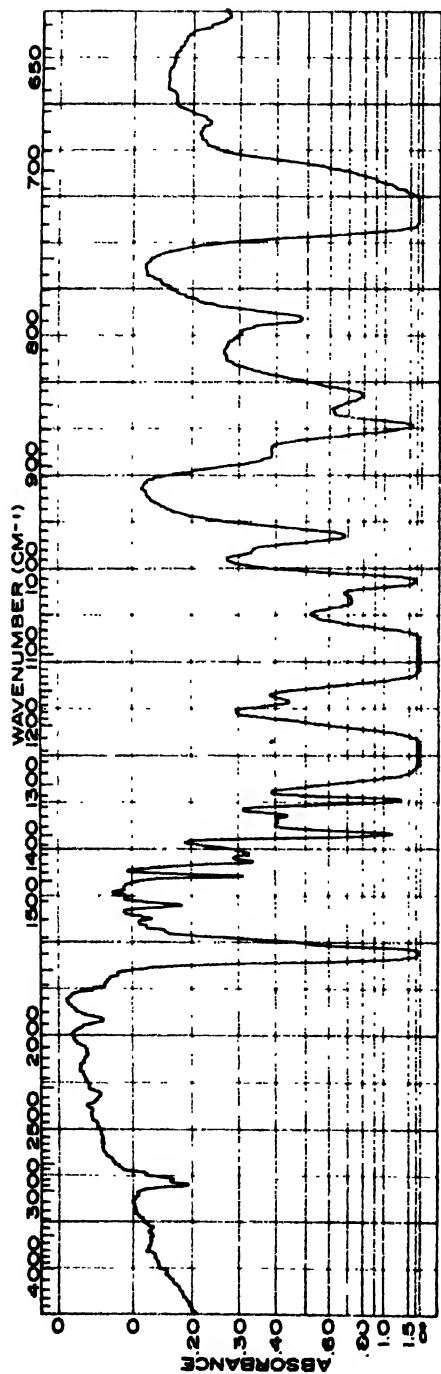
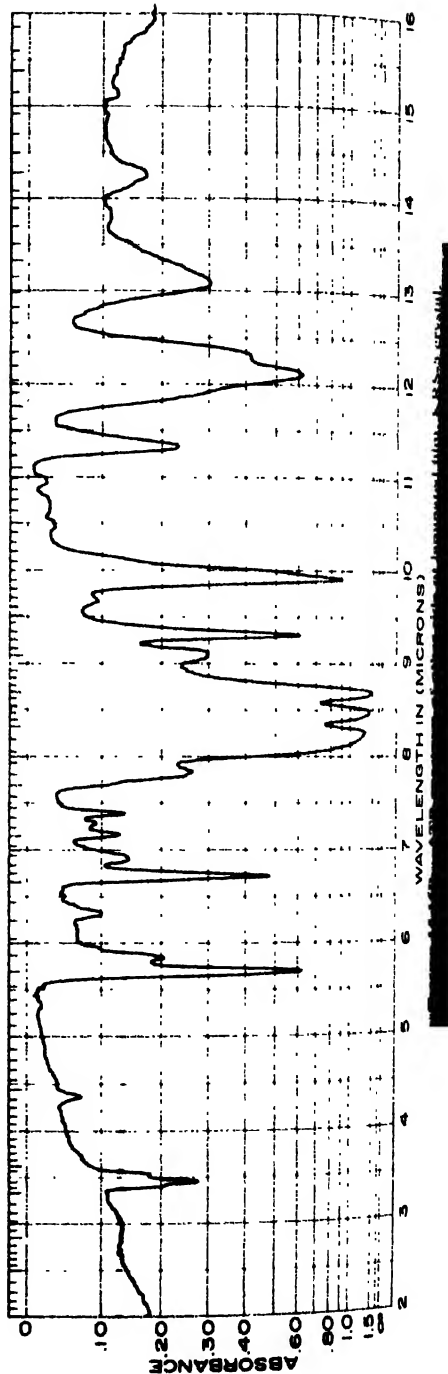


FIGURE 15-16A. ATR spectrum of one side of laminated film, KRS-5 crystal.



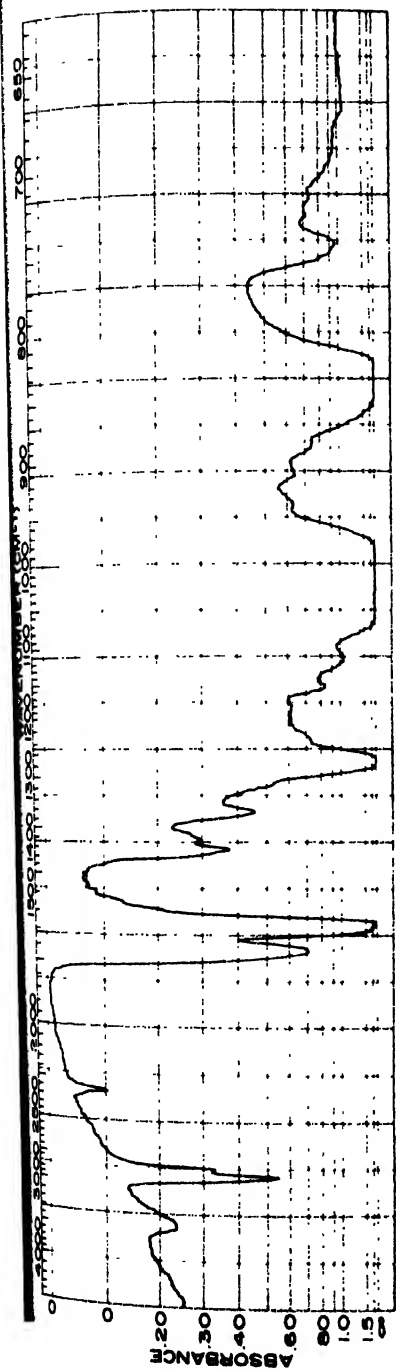


FIGURE 15-17A. ATR spectrum of cellophane wrapper from cigarette package, brand A, KRS-5 crystal, multireflection.

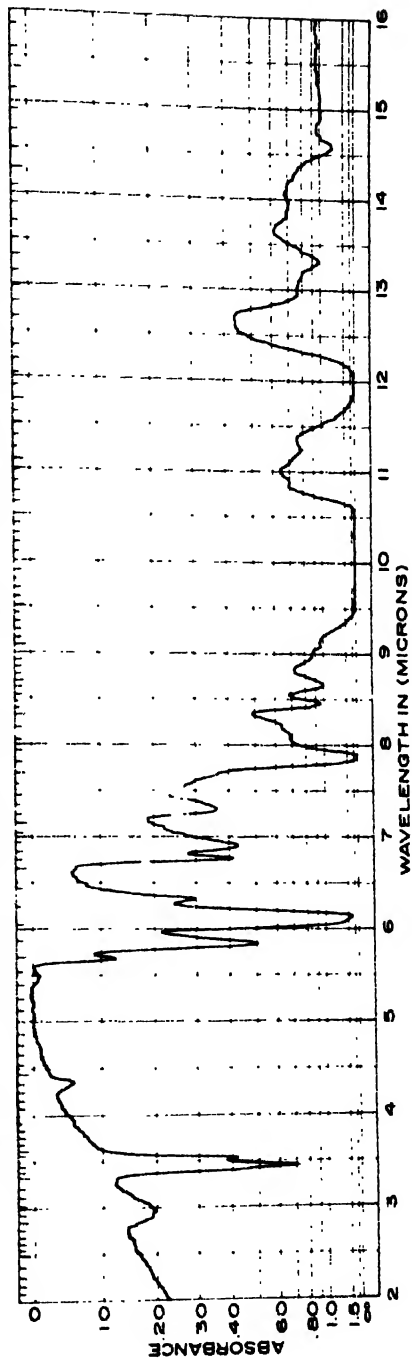


FIGURE 15-17B. ATR spectrum of cellophane wrapper from cigarette package, brand B, KRS-5 crystal, multireflection.

and new accessories have reduced this number. If one has the patience and is willing to try enough sampling variations and kinds and geometries of crystals, practically any sample can be made to yield an acceptable ATR spectrum. It should be emphasized, however, that ATR is but one of the techniques available to the spectroscopist. Do not use it when a simpler and easier technique will produce a satisfactory spectrum. Do use it when the simpler and easier procedures fail.

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CHAPTER

16

Microsampling Techniques

*David N. Kendall**

INTRODUCTION

When the quantity of sample available is sufficient to obtain an optimum intensity spectrum using macrosampling techniques, the normal sampling procedures described in Chapters 4, 6, 7, 10, and 15 are employed. In some fields to which infrared is applied, such as pharmaceuticals, biologicals, and general organic synthetic work, the spectroscopist is sometimes sample-limited. Or from any field of application infrared investigation may be necessary on a solid, liquid, or gaseous material too small to be sampled by ordinary techniques. Microtechniques must then be resorted to.

Strictly speaking, the prefix "micro" means one millionth of a unit of weight, volume, etc. To the practical spectroscopist, however, obtaining a mull on less than about 3 mg, a liquid spectrum on less than a drop, or a gas spectrum on less than 25 ml normally suggests the use of a microtechnique. There are exceptions, of course. If the sample is an extremely strong infrared absorber, macro methods may still be applicable with the size samples given above.

MICROSAMPLING FOR SOLIDS

The spectroscopist is presented with a black speck of solid taken from a miniature bearing. This black speck is believed the cause of an operational failure. "What is it?" is the question the engineer making the presentation asks. Observation quickly indicates it weighs less than 1 mg. In fact, only a

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look under 10X magnification convinces one the speck really exists. After the engineer has recited the possibilities as to the identity, such as oxidized oil or one of a number of nearby polymeric components, the investigator must decide. He can chance that the material is a very strong absorber and try a macrotechnique. Transfer the speck to a stainless steel vial, add, say, 299 mg infrared grade KBr, grind the whole with one or several stainless steel balls and prepare a 13 mm diameter disk approximately 1 mm thick in the normal manner to scan vs air. He might just as well start with a micro disk, however, for many times under the above conditions, the resulting spectrum will turn out to be a faithful reproduction of the moisture in the KBr.

Micro Pressed-Disks

The speck can be made into a 1.5 or 0.5-mm diameter pellet using commercially available micro KBr dies. About 4 mg KBr is normally used for the larger size pellet and about 2 mg for the smaller one. The pellet size is controlled by an opening of the desired diameter in the center of a 13 mm steel disk. The ground and mixed sample-KBr combination is placed in the orifice before pressing. For making 0.5 mm disks only the head, or evacuated portion of the die, is used. The vacuum used for evacuation is also used to apply the pressing force. For making 1.5 mm disks a small arbor press is sufficient, since only 500-lb pressure is required.

Refracting and Reflecting Beam-Condensers

The radiation beam area of commercial infrared spectrophotometers is considerably larger than the area of a 1.5 or 0.5-mm diameter disk. Typical beam areas are about 13 by 4 mm. One could mask off the beam to the area covered by such disks. The resulting loss of source energy, however, would be prohibitive. Therefore, a beam-condensing device is used to reduce the beam area at the sampling position. Two types commercially available are the refracting beam-condenser and the reflecting or mirror beam-condenser.

The refracting beam-condenser is less expensive, but has some disadvantages. Spherical convex lenses of KBr or AgCl are mounted on an appropriate framework. The total assembly is designed to be easily positioned in, or removed from, the sampling space of the spectrophotometer. The lenses are located on either side of the sample position. One lens reduces the beam area to 1 by 4 mm at the sample position; the other restores the beam to its original size for entry into the monochromator. This accessory is satisfactory for a 1.5-mm diameter pellet, but not the 0.5-mm diameter one. Its disadvantages include the chromatic aberrations of the lenses; the ready fogging of KBr in moist air, or the darkening of AgCl lenses when they are

used. When KBr or AgCl lenses are used with an instrument covering the rocksalt spectral range, however, the frequency region of most severe chromatic aberration is avoided.

Satisfactory qualitative spectra can be obtained employing a 1.5-mm diameter micro die and refracting beam-condenser on $1\mu\text{g}$ of a solid sample in favorable cases, i.e., with a very strong infrared absorber. In general, more reliable work is done with from 5 to $10\mu\text{g}$ of sample, since in the $1\mu\text{g}$ range it is almost impossible to distinguish a speck of sample from a speck of atmospheric dust.

The reflecting beam-condenser is more expensive, but has more advantages and fewer disadvantages by comparison with the refracting type. The mirror beam-condenser employing off-axis ellipsoidal mirrors can render a large image reduction ratio without spherical aberration. In a typical commercially available system, employing two 90° off-axis ellipsoidal mirrors, these condensing mirrors reduce the beam by a factor of six for focussing on the microsample and thereafter magnify the beam to fill the entrance slit of the monochromator. This accessory, mounted in the sample area of the instrument on a separate base plate for ready use or removal from the spectrophotometer, will accommodate the 0.5-mm diameter KBr disk. While $1\mu\text{g}$ of solid sample has been analyzed using this condenser and the 0.5 mm pellet, the analyst is more comfortable when $5\mu\text{g}$ of sample is available.

Beam Attenuators

Some loss of radiation is inevitable when either type of beam-condensing system is used. Maximum transmission with the system in proper alignment but with no sample in place will be 30 to 60% of the normal value. Since this energy loss is practically independent of frequency, i.e., "flat," compensation is possible. A piece of ordinary wire screen of appropriate mesh is placed in the reference beam to bring the transmission back again to 100%. It is convenient to have at hand a series of screens of different mesh for such purposes. Since some percentage of the radiation has now been prevented from entering the instrument, not enough power may be available to the pen servo system to produce a satisfactory spectrum. Therefore, the spectrophotometer slits should be widened to compensate for the energy loss. Some sacrifice in resolution will result, but this is usually not harmful when condensed phase samples are concerned.

If the spectroscopist wishes a device more elegant than ordinary wire screens for reference beam attenuation, commercial attenuators are available which are easily inserted in the reference beam sample space. They are readily adjustable to yield the degree of attenuation desired, and have the advantage that this accessory doesn't need to be removed when making a

normal scan with no attenuation whatsoever. The comb is readily removed from the beam without removing the attenuator from the instrument.

The 316 Micro Die and Pellet Holder

Recently Hewitt⁵ has designed an ingenious micro KBr die, shown assembled in Figure 16-1A and disassembled in Figure 16-1B. The pellet is pressed into a pellet holder, an integral part of the die, which doubles as an adapter. The holder, which contains the KBr disk, is provided with grooves and slides readily into the adapter sampling space so that the pellet is at the beam focus of the spectrophotometer. This model 316 Micro KBr Die and Pellet Holder needs no beam-condenser. About 45% of total energy is obtained with the empty pellet holder in place in the instrument. For most materials, spectra of satisfactory intensity will be obtained using 0.05 mg (50 μ g) samples. From 10 to 30 mg of KBr-sample mixture is used in pellet preparation. The die is evacuable to remove entrapped air from the mixture before pressing. Only 2000-lb pressure is required for a hold time of 15 to 20 sec. The finished pellet is 3/16 in. in diameter, and the total preparation time is 3 to 5 min. Prior to scanning, the 100% adjusting wedge is completely removed from the sample beam by turning the 100% T adjustment to the clockwise extreme. The reference beam is properly attenuated, as previously described, with a wire screen or other beam attenuator.

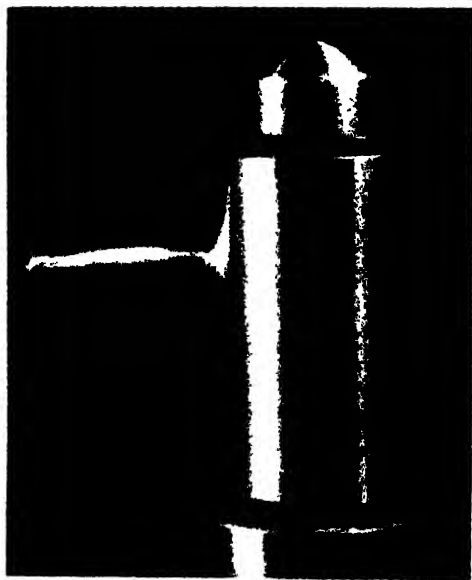


FIGURE 16-1A. Hewitt 316 Micro KBr Die and Pellet Holder, assembled.

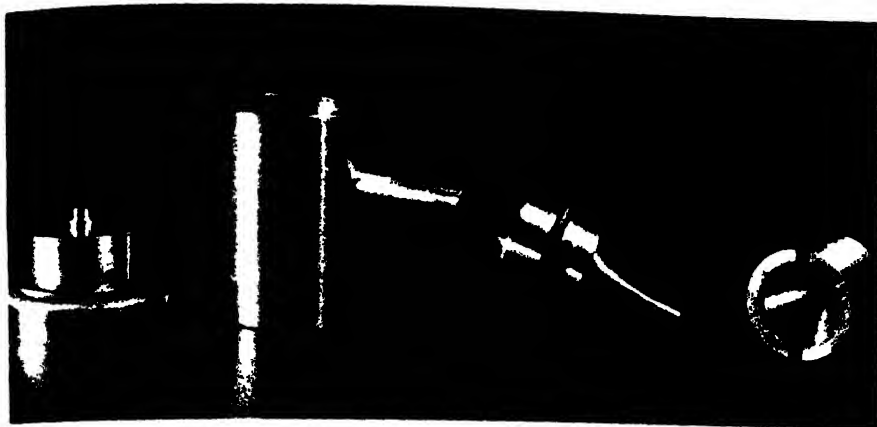


FIGURE 16-1B. Same die, disassembled.

Before attempting to use this micro die, a check should be made for proper alignment of the sample holder. After setting 0 and 100% T with air only in both beams, the empty pellet holder is slid into the adapter slot of the spectrophotometer. The 100% T adjustment is turned to its clockwise extreme. If the instrument is properly aligned, a reading of about 45% T should result.

The advantages of the Hewitt micro KBr die and pellet holder are that it requires no beam-condenser, the pellet does not have to be removed from the die for scanning, the pellet holder is made to fit the adapter slot of the spectrophotometer so that the pellet is at the best focus, and sample size requirement is less than one-seventh of that required for a macro 13-mm diameter disk.

Figure 16-2 shows the 2 to 15 μ region spectra of aspirin, benzoic acid, and bisphenol A scanned on pellets made using the Hewitt 316 Micro KBr Die and Pellet Holder. Each of the spectra represents a concentration of 0.1 mg of material in 20 mg of KBr.

The Freeze-Drying Technique

The difficulties encountered when employing microsampling techniques do not arise from optics, cells, or other accessories, but mainly from the problems involved in "finding," handling, and transferring very small samples. Here experience and ingenuity are a big asset.

When a solid microsample is large enough to be readily seen by the unaided eye, it can be transferred to a stainless steel vial and weighed on a good microbalance. The desired weight of infrared-grade KBr can then be weighed in the same vial, the whole mixed and ground, and the desired

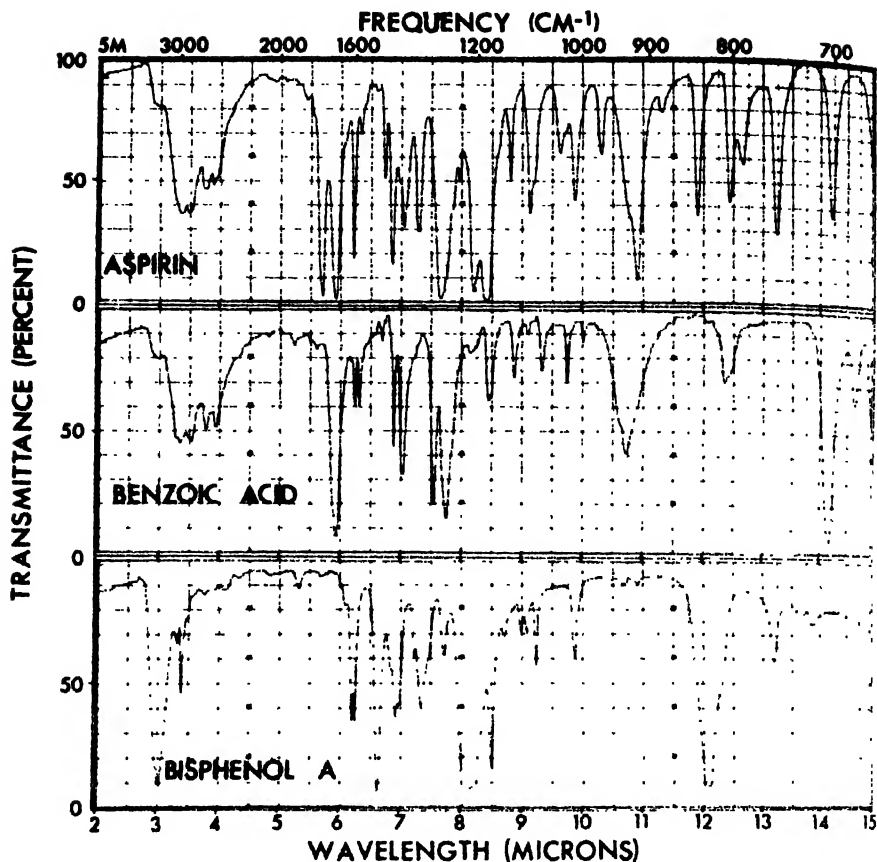


FIGURE 16-2. Spectra of aspirin, benzoic acid, and bisphenol A scanned on pellets made in the Hewitt Micro Die and Pellet Holder. For each, 0.1 mg material in 20 mg KBr

size micropellet prepared. Solid microsamples not so readily seen will require observation, handling, and transference using the magnification provided by an eye loupe or a microscope.

The lyophilization or freeze-drying technique is useful for both solid and high-boiling liquid microsamples. The KBr is dissolved in water, the solution transferred to a small tube whose opening is a male ground-glass joint. The tube is partially immersed in liquid nitrogen and the contents swirled so that the solution is quickly frozen and spread around the tube walls. The sample is then dissolved in any volatile solvent which will dissolve it. This solution is added to the tube, swirled, and flash frozen atop the water-KBr layer. A high vacuum system is now connected to the tube, and solvent and water pumped off while the tube remains in the

liquid nitrogen bath. This procedure leaves both the KBr and sample finely divided and well mixed. A micropellet is then pressed and the spectrum scanned. Since it normally requires several hours of pumping to remove the solvent and water, this technique is tedious and is normally used only when simpler procedures are not applicable.

Micropellets from Macro Dies

Spectroscopists having available only a macro KBr die which, e.g., normally makes a 13-mm diameter pellet, can try their hand at obtaining spectra from microsamples using a technique developed by Mebane.⁷ Grind and mix the solid sample at about 1% concentration in KBr. Make a 1 mm by 3 mm aperture in a 13-mm diameter disk of white blotting paper. Place 2.5 mg of the sample-KBr mixture in the aperture. Press between polished steel plates using about 25,000 lb total force. The pressed disk obtained, well centered, now fits into a standard 13-mm macro KBr disk holder and can be readily inserted via the adapter grooves at the focus of the spectrophotometer. Since the sampling area is now masked down to 1 mm by 3 mm with blotting paper, only about 25% T is obtained. To obtain a full scale spectrum, therefore, a 25% T screen is placed in the reference beam. Compensation for energy loss is achieved by using a wider slit program.

The Infrared Microscope Attachment

If the investigation of samples in the microgram and submicrogram range is desired, the beam-condensers previously described will not suffice. A compound mirror system must be employed and this is a more complex attachment to the spectrometer results. An infrared microscope attachment,⁴ which is commercially available, has been described employing the Schwarzschild microscope principle. The condenser and objective pair operate at a numerical aperture of 0.75, with a 0.4 obscuration ratio. They are designed to provide optimum imagery in the infrared region of the spectrum. The condenser forms an image of the exit slit at the sample space reduced 8.5X, and the objective provides a 25X enlarged image of the sample at an adjustable diaphragm. A viewing and manipulating system is provided to allow accurate positioning of small samples. The maximum field size is 0.650 by 0.220 mm. To minimize heating and photochemical effects from the intense radiation flux at the focus, the microscope attachment is mounted after the exit slit of the monochromator in the dispersed beam. About 35% of the radiation available from the monochromator is conserved by utilizing field mirrors to provide efficient energy transfer and minimizing the number of reflecting surfaces. The radiation is brought to a separate detector and preamplifier which are connected to the amplifier

and recorder of the spectrometer. This microscope is attached to single beam spectrometers, and the normal macro functions of the instrument are not disrupted. Convenient macro-micro conversion is provided.

In the operation of the microscope attachment, the size of sample necessary for obtaining useful spectra and the purity of the radiation striking the detector are critical. Sample size is restricted by limitations on both thickness and cross-sectional area. The required thickness is about the same as for macro work, i.e., about 25μ . The minimum sample area is that required to provide sufficient energy for satisfactory detection. It is inversely proportional to source brightness, transmission efficiency, detector detectivity, and the square of the effective numerical aperture of the microscope objective. The operator must strike a compromise between cross-sectional area, amplifier band pass and thus scanning rate, signal-to-noise ratio, and spectral resolution.

Because of the variety of factors affecting energy and their variation with wavelength, no single minimum sample area can be stated as the limit even for a single instrument. It is, however, possible to choose a set of reasonable operating conditions and state the area limit for these conditions. Working at 2μ , e.g., a minimum sample area of $600\mu^2$ is required with peak-to-peak signal-to-noise of 19, a 2.1 sec time constant, a spectral slit width of 34 cm^{-1} , with a sample length of 100μ and width of 6μ . The reader is referred to the original paper for a tabular guide to minimum sample area at other wavelengths.

It is necessary to take precautions to insure the purity of the radiation reaching the detector. If the sample does not cover the entire field of the microscope, some radiation will reach the detector without being subjected to absorption by the sample. This impurity radiation "dilutes" the spectrum and is especially important for long, narrow samples such as fibers. The microscope attachment described provides for the reduction of impurity radiation in several ways. The viewer system allows precise alignment of the slit image, sample, and diaphragm opening. The diaphragm is adjustable so that it can be made slightly smaller than the image. The large numerical aperture of the objective reduces the size of the diffraction pattern. The objective is free from coma, astigmatism, and chromatic aberration. The spherical aberration is $\frac{1}{4}$ wave at 2μ and becomes negligible at long wavelengths.

Using the microscope attachment, spectra have been obtained, e.g., of 25μ -thick adrenal sections of the cortex and medula of a normal rat, of 50μ -thick sections of the grey and white matter regions from the hypothalamus of a normal rat, of an acrylic fiber 17μ in diameter and a Nylon fiber 20μ in diameter. The spectra resulting were quite satisfactory for identification and other investigative purposes.

Capillary Absorption Cells

For the purpose of obtaining spectra from microsize samples, methods of fabricating, filling, and sealing capillary absorption cells from silver chloride, sodium chloride, and polyethylene have been reported.^{2,6,8} Black¹ has described a potassium bromide capillary cell which can be successfully used with the microscope attachment discussed above. Spectra in good agreement with those obtained on the macro scale can be scanned from 3 or 4 μg of nonvolatile samples.

A normal 13 mm diameter die is used for the fabrication of the capillary cell. Sufficient KBr to form a pellet 1 to 2 mm thick is used. Half this amount is compacted with moderate hand pressure on the bottom face of the partially assembled die. An L-shaped wire, shorter than the pellet diameter, is centered on this layer of salt, the remainder of the KBr added and hand pressed. The pellet is completed in the usual manner under vacuum and high pressure. The pellet is then cut with a razor blade perpendicular to the L-shaped wire just inside either extremity of the wire. The first cut can be made without breaking the wire. One arm of the L is thus extricated. The second cut opens the other end of the capillary. The wire is withdrawn by grasping it with flat-faced pliers or forceps. Rubber finger cots are worn to prevent fogging of the pellet.

Capillaries 0.075 mm in diameter can be formed with No. 40 Chromel A wire. A snapping pull of this wire breaks it into straight sections, burr-free at one end, that are suitable for the L-shaped wires. The final length of the 0.075-mm diameter capillary is usually 7 to 8 mm.

Black found that the microscopic imperfections evident throughout the pressed salt capillary do not interfere with obtaining satisfactory spectra. A solid portion of the pellet serves as a background against which to compare a spectrum of a liquid in the condensed phase, because of the loss of transmission at the opaque curved sides of an empty capillary.

When sufficient nonvolatile sample is available, it can be transferred to the capillary without specialized equipment. For a micro-sized solid or nonvolatile liquid sample having appropriate solubility, about 0.05 to 0.10 ml CCl_4 can be added and the solution taken up in a micropipet. For final concentration, the solvent of the solution is evaporated dropwise on a smooth nonwettable surface such as flat "Teflon" film, 0.006 mm thick, stretched over a 3/4 in. hole in a metal or plastic plate and secured with tape. As evaporation proceeds, the concentrate agglomerates in a small area. At the appropriate concentration, when 3 to 4 μg of solute in CCl_4 solution will end up in the capillary, the sample is introduced into the capillary by touching the end of it to the solution on the film. The capillary can then be sealed, e.g., by the rapid, firm pressing of molten polyethylene to the ends of the freshly filled capillary. Glass rods, 3 to 4 mm in diameter,

which have been standing in a few millimeters' depth of the molten plastic at about 125°C are used. The melt solidifies instantly on the KBr surface and makes an effective seal, as indicated by a clear, glassy appearance of the polyethylene. A good polyethylene seal still allows very gradual evaporation of CCl_4 . Such, however, is slow enough to give ample time to record the spectrum. Occasionally, loss of solvent over a period of hours or overnight allows spectra to be obtained at different concentrations and eventually in the condensed phase in the same capillary.

The KBr capillary cell technique provides for ease of location and focusing in the microscope, good clarity of the absorption cell unaffected by visual light and good transmission from 2 to 15 μ . Partial recovery of the sample is easily made by dissolving in water and subsequently extracting with organic solvent.

A Micromull Procedure

The lower limit to sample size for preparing a macromull is about 5 to 7 mg. And preparing a satisfactory mull with only that size sample available requires careful work. Techniques for spectroscopic work on 0.1 mg and even 5 μg of solids have been reported.³⁻⁹ These procedures require a beam-condenser and/or a microscope attachment on the spectrophotometer, which accessories have been already described in this chapter. A micromull procedure requiring only 0.3 to 0.5 mg of sample and no accessories to the spectrophotometer, was developed by Szonyi and Craske.¹⁰ Rocksalt windows 6 by 22 mm are used. A droplet of paraffin oil, about 0.005 ml, is placed on one of these windows from a microsyringe. The solid sample is dissolved in a volatile solvent to yield an approximately 1% solution—e.g., 0.5 mg in 0.05 ml. About 0.05 ml of this solution is then transferred dropwise to the oil droplet using a microsyringe, allowing time for the solvent to evaporate after application of each drop. A mixture of the solid and paraffin oil only remains on the plate. This mixture is then homogenized by pressing a second rocksalt plate atop the first. The spectra obtained by this technique are equivalent to those obtained on paraffin oil mulls prepared by the normal macrotechniques.

Microsize solid samples can also be studied spectroscopically through use of the techniques described in Chapter 14.

MICROSAMPLING FOR LIQUIDS AND SOLUTIONS

Microcells for Liquids

For volatile liquids or solutions requiring volatile solvents, satisfactory spectra can be obtained on from about 10 to 100 μg of active material using a liquid state microcell. A number of such cells are commercially available.

Typically, such a cell with an 0.025 mm spacer has a volume of $1\mu\text{l}$; a 3 mm spacer results in a volume of about 0.05 ml. A long needle tip is soldered to the cell body. When the needle tip is immersed in a liquid while the cell body is held below the liquid level, the sample will rise in the needle by capillary action, and fill the cell space. The needle tip is sealed by inserting it into a piece of rubber or "Teflon." Provision is normally made for the liquid microcell to be inserted into the sampling space of the spectrophotometer at, or very close to, the beam focus.

Microsize Nonvolatile Liquids

If a microsample is nonvolatile liquid insufficient in volume to fill a liquid microcell, it can be dissolved in a volatile solvent. The solution is now used to wet some finely ground infrared-grade KBr powder. During the mixing and grinding step in the preparation of a disk, the heat developed will usually serve to eliminate the volatile solvent. The microsize disk is then prepared in the normal manner, scanned, and the spectrum of the nonvolatile liquid obtained. Some spectroscopists carry out this whole operation in the pressing die.

Gas Chromatograph Fractions

Collecting microsize cuts from gas chromatographs for infrared identification purposes is of growing importance. If liquid fractions can be obtained by using a glass tube with a liquid trap as a micro dewar, they can be transferred to a liquid microcell for scanning. Commercial instruments and accessories are available for scanning gas chromatographic fractions as they are eluted in either the gaseous state or by condensing them to liquids. A rapid 45 sec scan time, covering the 2 to 15μ range, enables most materials to be identified from the spectra resulting, provided the chromatographic fractions don't come off too closely spaced.

MICROSAMPLING FOR GASES

If as much as 25 ml of a gaseous sample is available, e.g., from a gas chromatograph effluent, then macrosampling procedures can be employed, using a 7.5 cm path length, 25 ml volume gas cell. Such small volume cells are constructed so that the inside dimensions are tapered to the light path. A typical commercial cell of this type has an aluminum body and $\frac{1}{4}$ in. pipe taps with standard metal nipples for fitting flexible hose. This cell can be evacuated to a few microns Hg pressure and can be pressurized to about 800 mm/Hg.

When less than 25 ml of a gas sample is available, then multi-reflection gas cells are necessary unless the gas is such a strong infrared absorber

that one of the commercially available, small volume, short path-length gas cells can be used. Typical minimum volume cells, e.g., require a 16 ml sample for a 7.5 cm path length and a 6 ml sample for a 5 cm path length.

A microgas cell requiring a volume of 22 ml and capable of a path length of 1 meter by 24 passes through use of multiple reflections has been described.¹¹ This cell requires an auxiliary beam-condensing system, and the overall transmittance of the microgas cell and associated microscope accessory is about 30%. This energy loss is compensated for by methods previously described. The cell can be heated up to 250°C to keep a sample of low volatility in the vapor phase so that it will not condense out during scanning of the spectrum. Satisfactory spectra have been obtained on as little as 0.1 mg sample weight using this cell. How low a sample size can be successfully handled in this microgas cell depends, of course, on the inherent absorptivity of the gas under investigation.

When the spectroscopist has available only 1 to 5 ml, or less, of a gas sample, mass spectroscopy and/or gas chromatography should be resorted to. These techniques, particularly in combination, are the most powerful and convenient to use on small volume gas samples.

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CHAPTER

17

Inorganic Applications of Infrared Spectroscopy

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INTRODUCTION

The application of infrared spectroscopy to inorganic compounds has developed much more slowly than its use on organic materials. This was perhaps to be expected, since all organic compounds yield infrared spectra but some inorganic materials do not. Inorganics such as NaCl, KBr, LiF, CaF₂, CsBr, CsI, and KRS-5 (thallous bromide-iodide) were found, over the course of the history of infrared, to make excellent prisms and windows for various spectral regions. Monatomic elements, monatomic cations and anions do not absorb infrared. Neither do inorganic compounds comprised of monatomic cations and monatomic anions. Polyatomic ions, however, do exhibit characteristic infrared spectra. Therefore, infrared has widespread usefulness in the field of inorganics for identification purposes and in the study of coordination compounds and complex ions.

Classification of Vibrations in Crystals

Crystalline materials may be conveniently classified into three broad groups: ionic solids, molecular solids, and covalent solids. For ionic solids consider first those comprised of monatomic ions only, such as sodium chloride, potassium bromide, and lithium fluoride. The only vibrations of these crystals are "lattice" vibrations, in which the individual ions undergo translatory oscillations. The bands resulting from these oscillations are broad and are responsible for the long-wavelength cutoff in transmission. Sodium chloride, e.g., cannot be used as a prism or window beyond 15 μ .

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For ionic solids containing polyatomic ions, such as ammonium chloride or calcium carbonate, lattice vibrations also include rotatory oscillations, but in addition, internal vibrations occur. These latter are primarily the distortions of molecules whose centers of mass and principal axes of rotation are at rest. The internal vibrations are characteristic of each specific kind of ion and arise because of the covalent character of the binding together of the atoms comprising the polyatomic ion.

Molecular solids are uncharged molecules held together in the lattice by weak forces of the van der Waals type and often also by hydrogen bonds. Benzene, phosphorus, and ice are examples of this type of crystallinity. Such solids also undergo both lattice modes and internal vibrations, and because of the latter yield characteristic infrared spectra.

In covalent solids, such as quartz and diamond, the whole lattice is held together by covalent bonds. Therefore, the distinction between lattice and internal vibrations disappears. Covalent solids yield absorption spectra with very characteristic bands. They are in some ways analogous to polymers, which in spite of their size and complexity give unusually discrete spectra.

Sampling Techniques

In general, the same sampling procedures can be employed with inorganics as for organics (see Chapter 4). While solids may be studied in solution, with most inorganic samples there is considerable difficulty in finding suitable solvents. Some salts are soluble in partially chlorinated solvents such as methylene chloride or chloroform, but caution must be observed in the interpretation of results since there is generally considerable interaction between the solvent and the solute. In fact, these solutions are often studied with the intent of evaluating such interactions rather than to study the solute itself.

Covalent inorganics may be studied in any organic solvent in which they are soluble provided the spectrum of the solvent does not obscure spectral regions of interest of the molecule under observation. Metal carbonyl derivatives are often soluble in organic solvents, and are generally studied in solution where the possibilities of resolution of infrared bands are greater than in the solid state.

Water is the most common inorganic solvent. Because of the rather limited range of infrared transparency, for water, the special cells required, and the rather high solute concentrations, infrared studies on aqueous solutions have not been widespread. It offers a fertile field for further exploitation, especially with respect to biological systems.

Since most inorganic compounds are solids, the most widely used sampling techniques are the mull and the pressed alkali halide disk methods.

Inorganic gases are handled by the usual gas sampling procedures. Care must be taken to select cell windows and cell bodies of materials which will not react with the gases being investigated.

APPLICATIONS OF INFRARED TO INORGANICS

Early Work

Schaefer and Matossi¹⁹ reviewed the infrared work done on inorganics up to 1930, most of which concerned reflection spectra. Lecomte and co-workers¹⁰ made extensive surveys of the infrared absorption spectra of inorganics but much of their data were taken prior to the advent of modern spectrophotometers. Studies on a few ions are related in the classic works of Herzberg⁶ and Wu.²² Halford,¹⁵ Hornig,²¹ and their co-workers have carried out detailed studies of the spectra of selected compounds. The widely used Colthup spectra-structure chart⁴ lists characteristic absorption frequencies for ammonium, carbonate, nitrate, phosphate, and sulfate. Hunt, Wisherd, and Bonham⁷ were the first to present a compilation of infrared spectra of inorganics scanned on a modern spectrophotometer. Their collection of the spectra of 64 naturally occurring minerals and rocks included the spectra of 16 related inorganic compounds. It is a very useful reference collection for the identification of fillers and the like in plastics, coated papers, and other formulations.

Survey of Spectra

Miller and Wilkins¹² carried out the first extensive survey of the infrared spectra of inorganic compounds. Their excellent and widely-used collection covers the spectra of 159 pure inorganic compounds, principally salts of polyatomic ions. A table of characteristic frequencies for 33 polyatomic ions is given, covering the 2 to 16μ (5000 to 625 cm^{-1}) region. They found the quality of the spectra of inorganics ranged from surprisingly good ones with sharp intense bands, e.g., barium thiocyanate dihydrate, to very poorly defined ones such as that of potassium silicate. Phosphates, most particularly their monobasic and dibasic salts, characteristically yielded ill-defined spectra. In general, however, most of the polyatomic ions studied were found to exhibit characteristic frequencies. These were distinctive and did not show a large spread in wavenumbers. Therefore, these characteristic frequencies are useful in the qualitative analysis of inorganic unknowns.

The effect on the vibrational frequencies for polyatomic anions of varying the positive ion was studied by Miller and Wilkins. Ten sulfates and ten nitrates were examined. The sulfates all showed two characteristic frequencies, one of medium intensity between 610 and 680 cm^{-1} , the other of strong intensity between 1080 and 1130 cm^{-1} . No orderly relation between

the positions of the sulfate bands and a property of the positive ion was evident. There is, however, enough variation among the spectra of the individual sulfates so that it is often possible to distinguish among them from the exact positions of their absorption bands. This is most readily done when comparing spectra of individual sulfates against each other. It is not possible, however, to tell from the spectrum of an unknown mixture, in which a sulfate is only one of several components present, whether one is confronted with sodium sulfate or potassium sulfate. For a number of the sulfates, though, identification in a mixture situation is possible.

The nitrates showed characteristic frequencies between 815 and 840 cm^{-1} of medium intensity and between 1350 and 1380 cm^{-1} of very strong intensity. No orderly relation between the positions of these nitrate bands and a property of the positive ion, such as its charge or mass, was found.

Hunt, Wisherd, and Bonham,⁷ on the other hand, found that for anhydrous carbonates there is an approximately linear relationship between the wavelength of the characteristic 11 to 12μ band and the logarithm of the mass of the positive ion(s). Hunt observed that Miller and Wilkins' data fit this curve, with the exception of lithium carbonate.

It is probably not surprising that for most salts of polyatomic ions there exists no simple orderly relation between the locations of the characteristic frequencies and some property of the positive ion. Differences in the type or extent of hydration very probably change some of the frequencies. Changing the positive ion can produce a different crystalline arrangement which alters the symmetry or intensity of the electrical field around a negative ion. Positive ions of the same charge but varying radii will produce different electrical fields in the various salts exerting varying effects on the vibrational frequencies of the negative ions. And similarly for positive ions of different charge but the same radii.

Miller and Wilkins assessed the usefulness of infrared to the qualitative analysis of unknown inorganic mixtures both alone and in conjunction with emission and x-ray spectroscopy. Infrared proved particularly valuable for noncrystalline materials and those which gain or lose water of hydration readily. To such substances, x-ray analysis is normally not applicable, and it becomes difficult when applied to a complete unknown containing more than two components. Materials like metal oxides, hydroxides, and sulfides in general show no sharply defined infrared absorption between 2 and 16μ except for possible water and hydroxyl bands. Such substances are often good samples for x-ray analysis. The principal difficulty with emission analysis is its great sensitivity. It is often difficult to distinguish between major components and impurities.

The best sequence for using the combined techniques was found to be in the order --- emission, infrared, and then x-ray. The first two uncover

certain possibilities for metals and polyatomic ions present which greatly simplifies the interpretation of the x-ray data.

Infrared analysis has advantages over wet chemistry for detecting the more unusual ions not normally included in the usual analytical procedures, such as BO_2^- , $\text{B}_4\text{O}_7^{--}$, $\text{S}_2\text{O}_3^{--}$, and S_2O_5^- .

The spectroscopist should not be surprised to find that occasionally the spectra of two different samples of the same inorganic compound are somewhat different. The impurities present in the two samples may be different, accounting for the spectral differences observed; the spectra will be different if anisotropic crystals are involved and completely random orientation of the crystallites has not been attained for one spectrum or the other; if the spectra represent different polymorphic modifications of the same substance they will be different.

The frequencies characteristic of the salts of polyatomic ions carry over moderately well into complex ions. Potassium ferricyanide, e.g., has a band at 2100 cm^{-1} and three ferrocyanides show one near 2010 cm^{-1} . In simple cyanides this stretching frequency of the cyanide ion occurs between 2070 and 2080 cm^{-1} . The complex ion, $\text{Co}(\text{NO}_2)_6^{--}$, shows absorptions at 847 , 1335 , and 1430 cm^{-1} , while the corresponding frequencies for the nitrite ion are 820 to 835 , 1235 to 1250 , and 1328 to 1380 cm^{-1} .

Miller and co-workers¹¹ extended the earlier work of Miller and Wilkins in the NaCl prism region to the CsBr prism region. The spectra and characteristic frequencies of many common inorganics are presented over the 700 to 300 cm^{-1} region. Metal-Cl bonds, e.g., usually absorb in the 300 to 400 cm^{-1} range and Metal-F over the 400 to 800 cm^{-1} range so the extended wavenumber range covered is useful for studying and identifying certain inorganics.

A large amount of data concerning infrared absorption of inorganic substances has been presented by Lawson.⁹ While the data is largely unclassified and not complete, the spectroscopist requiring information on inorganics can consult this volume to learn whether it contains what he seeks.

Inorganics and Coordination Compounds

Nakamoto¹⁴ discusses the observed fundamental vibrational frequencies of inorganic compounds and coordination compounds in terms of their relation to molecular structure. A wealth of data is given on inorganics classified by the number of atoms in the molecule and molecular geometry, e.g., diatomic molecules, linear triatomic molecules, bent triatomic molecules, pyramidal four-atom molecules, planar four-atom molecules, etc. In addition to the listing of fundamental frequencies for many compounds, 16 complete or partial spectra are included on inorganics. The section on

coordination compounds covers ammine and amido, nitro and nitrito, lattice water, aquo and hydroxo, carbonato, nitrato, sulfato and other acido, cyano, rhodanato, azido, carbonyl, nitrosyl, urea, sulfoxide, ethylene diamine, alpha-diimines, dimethylglyoxime, carboxylic acid, oxy-acid, alcohol, amino acid, ethylenediaminetetraacetic acid (EDTA), oxalic acid, acetylacetone, and other miscellaneous complexes. Most metallo-organic compounds are purposely omitted from the discussion. About 70 complete or partial spectra of coordination compounds are given in addition to a listing of observed frequencies for many complexes.

Determination of Inorganics in Polyvinyl Chloride Formulations

As previously discussed, infrared can be successfully used to identify unknown mixtures of inorganics containing polyatomic ions, in favorable cases. And in conjunction with emission and x-ray analysis a greater variety of such mixtures can be identified. Furthermore, the spectroscopist often faces the situation where only one or two inorganics are present and require qualitative analysis. Such is true, e.g., of the components in polyvinyl chloride (PVC) formulations. PVC compounds are used in a wide variety of products, electrical insulation for one, and are therefore formulated to provide a wide range of physical properties. The physical properties required in a compound depend upon the product in which it is used. These properties are largely determined by the type, the quantity, and the quality of the compounding ingredients. In addition to PVC there is normally present in these formulations plasticizers, stabilizers, and fillers. Since the plasticizers and PVC are organic and the fillers and stabilizers essentially inorganic, component separations can be made, leaving usually one filler and one stabilizer, as a dry powder, requiring identification. More than one filler or stabilizer may be present, of course.

First the plasticizer is solvent extracted from the finely divided PVC formulation using a Soxhlet extraction apparatus and either ethyl ether or carbon disulfide as solvent. The stabilizers and fillers are then separated from the resin by dissolving the latter in warm tetrachloroethane followed by a wash with hydroquinone-free tetrahydrofuran and centrifugation. After oven drying, the stabilizer and filler remain as a dry powder. If color pigments and carbon black were components of the formulation, they will usually remain in the stabilizer and filler fraction. Ordinarily the concentrations of colorants including carbon black will be low in relation to the filler and stabilizer content. Therefore, the former will not prevent spectral identification of the latter. It should be borne in mind that organometallic or organic stabilizer, if present, may partially or wholly separate with either the plasticizer or resin components and should be considered during the infrared examination of these components.

The stabilizers and fillers can be identified by scanning either as mulls or a KBr pellet. Quantitative procedures can often be successfully set up for these components, following qualitative infrared analysis. Typical stabilizers present, e.g., in electrical grade PVC formulations, may be basic lead carbonate, dibasic lead phosphite, dibasic lead phthalate, normal lead salicylate, basic lead silicate sulfate, basic lead sulfate, dibasic lead stearate, or lead silicate-silica gel complex. Calcined clay and calcium carbonate are typical examples of fillers.

The American Society for Testing and Materials (ASTM) has published a general method for the infrared spectrophotometric analysis of components in PVC Compounds,¹ which includes qualitative as well as quantitative procedures for determining stabilizers and fillers. The quantitative method suggested employs the KBr pellet technique. Beer's Law plots are prepared from scanning standard samples made up by mixing the pure compounds of interest in appropriate amounts to give a set of matched standards. The absorption bands listed in Table 17-1 can often be used as analytical frequencies:

TABLE 17-1.

Component	Analytical Frequency, (cm ⁻¹ , wavelength, μ)	
Basic lead carbonate	1410	(7.09)
Calcined clay	1075	(9.30)
Calcium carbonate	877	(11.40)
Antimony oxide	741	(13.50)
Basic lead sulfate	1130	(8.85)
Dibasic lead phthalate	1535	(6.51)

Consider a PVC formulation, e.g., in which the only stabilizer present is basic lead carbonate and the only filler is calcined clay. After separation of this stabilizer-filler mixture from the other components of the formulation, as previously described, a KBr pellet may be prepared containing 0.1% of this mixture. By mixing 15 mg with 285 mg of KBr in a Wig-L-Bug for 3 min, a master batch is prepared. Then 16 mg of the master batch is mixed with 784 mg KBr in the same manner. The 800 mg pellet is pressed in a half inch diameter evacuable split cone die. A 2 minute evacuation time, to remove entrapped air, precedes the 2 minutes pressing time at 100,000 psi, with evacuation continuing. After scanning the resulting pellet over the 1800 to 950 cm⁻¹ spectral region, the base-line technique is used to measure the absorbances of the carbonate band at 1410 cm⁻¹ and the silicate band at 1075 cm⁻¹. The relative amounts of basic lead carbonate and clay

are then determined by reference to a calibration curve prepared with mixtures of known composition.

Burley and Bennett² present the 4000 to 650 cm^{-1} spectra of ten stabilizers and fillers commonly used in electrical grade PVC formulations. They also show the spectra of PVC prepared as cast films from five different solvents, emphasizing the fact that residual solvent is usually present in air-dried films, and that tetrachloroethane is the best solvent for identifying and quantitatively determining PVC or copolymers of PVC with polyvinylacetate. Also given in their paper are the spectra of four commonly used plasticizers.

Carbon black is sometimes added in amounts of 1% or less to PVC formulations as an ultraviolet light screen or colorant. During the analysis of the components of a formulation, the carbon black becomes distributed between the resin, and the stabilizer and filler. If necessary, it can be removed from the resin by filtering the resin solution with "Celite Filter Aid."

Inorganic pigments are separated with the stabilizer and filler portion and a number of such pigments can be identified from their infrared spectra. The collection of pigment spectra published by the Infrared Spectroscopy Committee of the Chicago Society for Paint Technology⁸ is very useful in this respect. The 2 to 15 μ spectra of 35 pigments are included in this compendium. This useful booklet also presents the spectra of 11 extenders, two anti-skinning agents; two driers; two surfactants; 22 solvents; 10 plasticizers; 20 oils and fatty acids; two silicones; 15 hydrocarbons, rosins, and miscellaneous resins; six cellulose; three isocyanates; two polyamides; three aminoplasts; four phenolics; five epoxy resins; five butadienes; 14 vinyl resins; 11 emulsions; four acrylates; and 17 alkyds and polyesters. In addition it contains helpful sections on elementary infrared theory, sample preparation, the preparation and care of windows and cells, qualitative analysis, quantitative analysis, research applications, and 259 literature references.

While a number of inorganic pigments can be identified from their infrared spectra, for others not yielding sufficiently characteristic spectra identification by emission spectrographic analysis should be resorted to.

Flame retardants in PVC formulations, such as antimony trioxide, may be identified by infrared methods, using the absorption at 740 cm^{-1} (13.50 μ), or by emission analysis. Chlorinated hydrocarbon flame retardants are extracted with the plasticizer and will be detected during infrared examination of the plasticizer fraction.

Determination of Bond Strengths

Much can often be learned about the bond strengths of inorganics, particularly inorganic complexes, through examination and correlation of

appropriate infrared spectra. While the vibrational frequencies are related to the individual bond strengths in a complex manner, and any fundamental treatment must consider the vibrations of the molecule as a whole, approximate approaches based on isolating certain vibrations often yield useful information.

Metal Carbonyls. In metal carbonyls, e.g., the bonding may be considered to be the sum of two parts. One is the overlap of an orbital on the carbon atom with an orbital on the metal atom to form a σ -bond in which electrons pass mainly from the carbon to the metal. The other part is the overlap of a d -orbital on the metal atom with a π -orbital on the carbon monoxide to form a π -bond in which electrons pass mainly from the metal into the ligand. The existing electron density in the ligand, and therefore the strength of the carbon-oxygen bond, will depend upon the relative amounts of these two types of bonding and will be affected by the type and electronegativity of the other substituents on the metal. Accordingly, the actual carbonyl vibrational frequency should reflect the number and availability of electrons in the remainder of the molecule. By observation of the carbonyl str region only, then, this number and availability of electrons can be compared. Table 17-2 shows the frequencies observed for some iron derivatives as given by Chatt, Pauson, and Venanzi.¹

TABLE 17-2. ABSORPTION MAXIMA IN THE CARBONYL STRETCHING REGION

Compound	Maxima (cm ⁻¹)
(C ₂ F ₅) ₂ Fe(CO) ₂	2160, 2120, 2100
Fe(CO) ₅ I ₂	2140, 2055, 2087
[Fe(CO) ₅ (C ₂ H ₅)] ⁺	2110, 2059, 1970
Fe(CO) ₅ (PPh ₃)I ₂	2095, 2050, 2035
Fe ₂ (CO) ₉	2087, 2023, 1831 ^a
Fe(CO) ₅ C ₂ H ₅	2050, 1995
Fe(CO) ₅	2028, 1994
[Fe(CO) ₅ H]	1996, 1972, 1897 ^a
[Fe ₂ (CO) ₉] ²⁺	1960-1935 ^b
[Fe(CO) ₄] ²⁺	1898

^aPeaks attributable to bridging carbonyl groups.

^bSingle maxima are observed; frequencies vary with the cation.

Hydrogen Bonding. Infrared spectroscopy is a powerful tool in the study of the strength of the hydrogen bond.^{16,18,20} When an M—H group forms a hydrogen bond M—H···N, there is a great change in the strength of the M—H bond which is reflected in the vibrational frequency of that bond. A nonhydrogen-bonded N—H grouping, e.g., absorbs from about 3500 to

3300 cm^{-1} , but when this group is hydrogen bonded to another atom, the frequency will be lowered, and may be observed as low as 2500 cm^{-1} or lower. That such bands arise from bonded N—H vibrations can be determined by deuteration studies. Study of ammonium salts has revealed that in the series NH_4F , NH_4Cl , NH_4Br , and NH_4I , the fluoride contains by far the strongest bond, as measured by the shift in the N—H frequencies. By contrast, infrared spectroscopy has shown the absence of hydrogen bonding in salts of the type NH_4MF_6 . Here there is no hydrogen bonding, or very little, because there is little charge on the fluorine atoms of the complex anion. The best arrangement for hydrogen bonding would be a linear N—H—F arrangement. Such a grouping, however, would cause a lowering of the electrostatic lattice energy because of the increased separation of the N and M atoms. Yet hydrogen bonding is present in compounds such as R_3NHF_4 . Here the N—H bond strength has become so weak that hydrogen bonding will stabilize the lattice.

Metal-Halide Bond Strengths. Peacock and Sharp¹⁷ have shown how infrared is applicable to the determination of metal-halide bond strengths. The MF_6^{4-} ion, e.g., gives rise to a series of vibrations which to date are too complex to allow calculations of force constants from the observed infrared absorptions. For similarly sized ions, however, the observed infrared frequency — an asymmetrical str frequency in an octahedral ion — follows closely the actual force constant which is, in turn, related to the bond strength. Table 17-3 illustrates the observed values for a series of complexes MF_6^{4-} . The relative frequencies follow closely the Irving-

TABLE 17-3.

Observed Infrared Frequencies for MF_6^{4-} Ions (cm^{-1})

Cr	Mn	Fe	Co	Ni	Cu	Zn
481	407	431	439	445	489	437

Irving-Williams Order for Stability of Complexes

Ionization Potentials $\text{M}^+ \rightarrow \text{M}^{2+}$

Cr	Mn	Fe	Co	Ni	Cu	Zn
16.6	15.7	16.5	17.3	18.1	20.2	17.9

Williams order for the stability of complexes, an order based on free energies rather than on bond strengths, and the appropriate ionization potential of the metal ion which is related to the covalent character in the M—F bond. In spite of the approximations which were made at all stages, the agreement among the series is seen to be good.

Molecular Weights of Unknown Polyethylene Oxide Derivatives

Levins and Ikeda¹¹ developed a simple, direct potentiometric titration for polyethylene glycols (PEG's) and their derivatives using sodium tetraphenylboron (NaTPB) as titrant in the presence of barium ions. A combined titrimetric and gravimetric procedure demonstrated that PEG's 600 to 4000 react stoichiometrically to form complex precipitates containing 2 moles of TPB and 10.4 ± 0.2 moles of ethylene oxide for each mole of barium. In the course of the method development, these investigators found that the approximate molecular weight of an unknown PEG may be obtained from the infrared spectrum of its complex precipitate. Nujol mull spectra were scanned on NaTPB, and various 2TPB.Ba.n PEG precipitates. A plot of the molecular weight of the parent PEG vs the absorbance ratio of the 9.2μ , 14.1μ bands yielded a smooth curve, from which it is possible to determine the approximate molecular weight of an unknown PEG. The graph obtained covered the range of PEG's from 400 to 10,000. The 9.2μ band used is the PEG ether str frequency and the 14.1μ absorption arises from the substituted phenyl ring of TPB. Levins and Ikeda found the titration described to be applicable to other polyethylene oxide derivatives, also.

Additional Applications

Infrared spectroscopy is applicable to the study of many inorganic problems for structure determinations; the quantitative understanding of the observed splitting of absorption bands in crystal spectra; the explanation of the frequency shifts between gas and solid phase spectra; the identification of new molecular species using the matrix isolation technique for suspending photolyzed molecules at temperatures of 5° to 40°K in rare gases; the study of solid surfaces with or without adsorbed molecules; solvent effects on band intensities, positions, and shapes; the origins of group frequency shifts; and information obtainable from the spectra of fused salts and highly associated liquids.

The reader interested in inorganic applications of infrared can follow the developments in the field by reference to the current literature. Of great help in this regard are the biennial reviews of infrared spectrometry appearing in *Analytical Chemistry*, the most recent one being by Evans.⁵

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CHAPTER

18

The Use of Computers in Spectroscopy

*Abraham Savitzky**

PROLOGUE

In discussing the use of computers in absorbance spectroscopy, I have found that too many people have a preconceived notion about this topic. They equate computers and spectroscopy with the library search system developed by L. E. Kuentzel in 1951^{1,2}, often called the ASTM IBM card system. Under this system, volunteer groups have searched the literature, taken note of the positions of major bands, and coded the information, together with some chemical information, onto IBM cards. These cards constitute an index of the spectra in the literature, and searching the index is an aspect of information retrieval (see Section 2 of this chapter).

Section 1 covers an entirely different aspect of spectra — the study of the individual curves themselves. Its subtitle might properly be "Curves and Computers." The reader must set aside all notions of library search for the identification of unknowns, since this is *not* covered in Section 1.

Section 1. Numerical Processing of Spectral Data

INTRODUCTION

The discussion in this section is based on the premise that there is a very large amount of information in the data which can be obtained from existing spectrophotometers, but that this information is being very incompletely

*The Perkin-Elmer Corporation, Norwalk, Connecticut.

used. Not that the current usage is ineffective -- on the contrary, the wide acceptance of spectrophotometric methods and instrumentation is ample testimony to the usefulness of the present techniques. But it does seem wasteful to run a spectrum and say "oh, that's polystyrene," and having identified the material, put the spectrum aside. It is only a short step to obtain still more information in the spectrum (the functional groups, etc.) and for many purposes, this is as far as it is necessary to go. But all this is purely qualitative information. Quantitative information taken from the usual curve would probably consist of laying down a baseline and reading the peak, or even several peaks. Sometimes there have been force constant calculations based on band position and integrated spectra, with pros and cons on their usefulness, etc.

Returning to the premise -- *if* there is more information, it must first be extracted, and then something must be done with it -- otherwise, it's useless. There are probably many ways of treating this information, but we shall arbitrarily decide to treat it numerically.

Why numerically? Primarily because the handling of numbers today is not the chore it was only a few years ago. One has only to read the papers, or indeed look around his own organization, probably in the accounting departments, to see staggering amounts of data being handled with no strain.

A spectrum, as we shall develop, can contain staggering amounts of data. To handle the data numerically, the spectrum must be in numerical form. This section will cover:

- (1) obtaining the data
- (2) some of the mechanics of processing that data in computers, and
- (3) using the data and computers to get meaningful information.

The first topic is called digitizing, the second is programming, and third is, of course, spectroscopy.

The use of digitizers and digitized spectra is not new. For example, G. W. King discussed information theory and spectra in an excellent series of articles in the *Optical Society Journal* starting in 1951.^{22, 23, 24, 25} Billmeyer,⁹ at Du Pont, applied a digital system to a spectrophotometer for color work. Rogoff and Taplin³⁶ at the Federal Telecommunications Laboratories developed a complete digital analysis system and so on. Somewhat more recently, Brackett,⁹ at the National Institutes of Health, and Johnson,¹⁷ at Du Pont, have reported work with digitizers which produced data to be analyzed on general purpose computers.

If we examine the history of these systems and try to consider the reason for the initial slow rise, and the much greater interest shown recently, we see that it coincides with the enormous changes in the computer art -- advances in the field of programming and in the availability and reliability of computers.

The scale of this availability is shown by a survey which reported over 5,300 computers delivered up to June 30, 1961, and over 18,409 delivered up to April 1964. While many of these are classified as "Business Data Processors," all digital computers, whatever their classification, provide the capability of handling extremely large quantities of numbers in any way we please, and at fantastically high speeds.

As an example of this, it is unlikely that anyone would like to tackle more than a 4 by 4 matrix on a desk calculator — and that's quite a chore. A small 1955 model digital computer solves a set of 10 simultaneous equations and prints the answer in report form, to several decimal places, in 14 min. Most of that time is consumed by the typing operation. A 1963 model computer, still small, can invert a 50 by 50 matrix in less than 30 sec.

Along with the growth in direct installations of computers has come a corresponding growth in service bureaus. If a machine is not available in one's own organization, it is possible to find computer time for rent within 100 miles of practically any large center. In general, the cheapest computer time is available on the most expensive computers since the user is most concerned with "computations per dollar" and not with actual machine rental in dollars per hour. Machine time is usually charged in hundredths of an hour.

PROGRAMMING

In some quarters programming is still considered to be a complex, mysterious, time-consuming operation. However, if properly approached, there is nothing magic, difficult, or time consuming about it.

Kinds and Definition

Basically there are two kinds of programming. One is characterized as computer-oriented programming, the other as problem-oriented programming. There is a thin line between them, but a most important one. The first looks upon the computer as an end in itself, "give me your problem, go away and leave me alone, and I'll give you the answer you want if you've defined the problem to me properly in the first place." The other says, "I have the problem, I know what the computer can or cannot do, and I'll go ahead and solve the problem." Of course there are all shades between the two. It has been said that it is easier to make a practical programmer out of a chemist than a practical chemist out of a programmer, and that is to be our viewpoint.

Programming can be easy or difficult, depending on how it is done. We must first define the term programming. A program for a digital computer is a restatement of a specific problem into a meaningful, highly formalized series of arithmetical and logical steps which the computer can follow in

order to arrive at the desired answer. You must translate your problem from terms which are meaningful to you into a program which is meaningful to the computer.

What a Computer Is and What It Can Do

What is meaningful to a computer? A computer is a high-speed, unimaginative clerical assistant. If properly instructed, a computer can add two numbers, subtract, multiply and divide. It can store a number in a specific location in its so-called memory and it can retrieve that information since the specific location is known. It can compare two numbers and determine whether one is less than, equal to, or greater than the other, and on the basis of this information it can be instructed to follow different paths — in other words, computers have both arithmetical and logical capabilities, and we shall discuss applications of both. Furthermore, computers can be instructed to read data in the form of holes in paper tape or punched cards, or magnetized spots on magnetic tape, or print data from information which has been stored or computed.

Machine Language and Problem-Oriented Language Programs

Machine language or symbolic language programs constitute a jargon very intelligible to the particular programmer who wrote the program, and to the machine, but still a problem to write, to read, and especially to debug — that is, to find the mistakes that inevitably creep into a gibberish of this type.

Actually, machine language programming is useful in special cases if one is willing to spend the time necessary to learn to cope with it. But the spectroscopist has problems to solve, and so he must use a problem-oriented language, a language which uses a somewhat formalized version of algebra and basic English to communicate with the machine.

These simplified programming methods use programs called compilers. The methods can be taught in a few hours. With their use, a program developed at one site for a specific computer can be easily converted at another site for use on an entirely different computer and can be readily understood by people with little or no formal training.

These programming procedures involve nothing more than setting down the series of steps in a rather restricted, but quite intelligible version of basic English, e.g., "READ A" means "take in data from a punched card"; "PRINT A" means "type the appropriate number"; a subscripted variable is referred to as "NU (I)"; and a logical instruction, written "IF (N) 20, 30, 40," instructs the computer to perform the operation called 20 if the value of "N" is negative, 30 if the value of "N" is zero, and 40 if the value of "N" is positive.

More complex problems, such as obtaining the inverse of a matrix, are solved by the use of procedures which have already been written in detail and are part of the computer program library. This particular problem is solved in our laboratory by writing into the program the instructions "CALL MINV (A,B)" where "A" is the name the programmer gives to the original matrix, and "B" is the name of its inverse. The compiler programs take these English language steps in the form described and translate them into appropriate, detailed instructions to be executed by the computer.

It is possible to become reasonably expert in these languages in 12 to 16 hr of instruction. The most common language in the United States is FORTRAN, in Europe it is ALGOL, and there are many variations of these depending upon the particular installation. A familiarity with any one of them will dispel the programming bugaboo, and translation from one to another involves only a reorientation in terminology.

Another simplifying aspect of programming is that many people have essentially the same type of problem—linear interpolation, a color analysis, a spectrophotometric matrix analysis—and programs already exist for their solution. Such programs are usually freely traded among machine users, and so they should be consulted as a first step in problem solution.

Obtaining Data in Digital Form

Now that the relatively minor problem of programming is settled, there remains the requirement of obtaining the data in digital form. The data from analytical devices are of two kinds:

The first kind involves single values relating to a particular sample: such measurements as pH, refractive index, melting point, burette reading, etc. These are two-dimensional for a group of samples in the sense that they are normally tabulated by sample number versus value. Within the table they are already in discrete, numerical form. The second kind are multivalued functions, such as spectra, chromatograms, and change of a single-valued function such as weight or pH, or optical density versus time, etc. These are two-dimensional for each sample, but they are continuous rather than discrete functions of the two coordinates, and this imposes special restrictions which will be discussed later.

In both of these cases, if the data are to be treated most efficiently in a digital computer, both coordinates should be encoded or digitized. While it is quite feasible to encode only the transmittance from a spectrometer at predetermined intervals, starting at a predetermined wavelength, this means extra care at the time every run is made, the entire record must be available to the computer at the time of processing, and a tear in the tape or momentary breakdown of the equipment could require the rerun of an entire experiment. These can sometimes be handled by writing the proper pro-

grams, but that shouldn't be necessary. If it is granted, then, that both coordinates of a system should be recorded, we can turn to the generalized description of a digital recording system.

The block diagram in Figure 18-1 shows the essential elements. Since the information desired is generally in the form of a voltage, a shaft position, or some other analog quantity, the input requires a pair of analog to digital converters (one for each coordinate). Each one may be voltage to digital or shaft to digital, depending upon the particular instrument configuration. The output of this system may be recorded on punched paper tape, magnetic tape, or punched cards. Punched cards are by far the least desirable from considerations of bulk, format restrictions, speed, and cost. The choice between paper tape and magnetic tape is made primarily on the basis of required sampling rate, cost, and operator convenience.

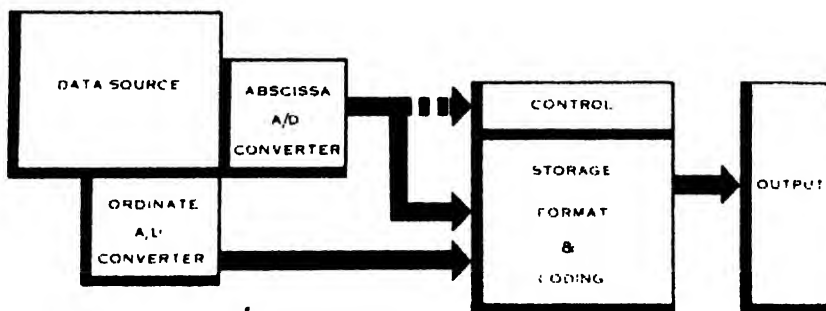


FIGURE 18-1. Block diagram of typical digital data recording system.

The function of the logic unit is to accept the data from the two digitizers, typically 5 digits for wavelength, 3 digits for transmittance, and organize it to be recorded 1 digit at a time by the output device. Since it is sometimes possible for the reading from the digitizers to change during the time required for recording the data, the storage unit has to be capable of storing "instantaneously" the entire 8-digit block of information and then recording it, digit by digit, in a format dictated by the particular computer being used. The function of the control unit is to recognize when a block of information is to be recorded - for example, when the wavelength changes by a predetermined interval, and to initiate the storage and recording cycle.

In today's spectrophotometers, the most useful A/D convertors are shaft encoders which are mechanically coupled to the wavelength drive and to the attenuator or recording pen drive. Installation is relatively straightforward, and if properly performed, places no restrictions on the normal operation of the instrument.

Once the curve is obtained in digital form it may be displayed again in graphical form on plotters which are found in most computer installations. All of the figures in this chapter were obtained in this way.

APPLICATIONS

In discussing the applications of digital computers in spectroscopy we shall proceed from the simple operations which extend the capabilities of the instrumentation, through operations on the spectrum or on libraries of spectra.

Smoothing a Curve in the Computer

In all spectrophotometers the basic design parameters set the fundamental signal-to-noise ratio of the instrument. For most applications, this is quite satisfactory. However, in certain situations, it is desirable to "push" the performance of the system to the utmost. This implies working at low signal-to-noise ratios, and at limiting resolution.

It is possible to reduce the noise in the spectrophotometer itself, but only up to a point. The more electro-mechanical filtering we introduce, the slower we must run; to reduce the noise by half, we must run one-fourth as fast. Once the point of diminishing returns is reached, all one does is introduce dynamic distortion errors into the spectrum. With the data in digital form, there are operations which can be performed which are completely free of any limitations placed on the electronics by real life condensers and resistors required in conventional filters.

Figure 18-2 is a stylized view of a section of a typical spectrum. The solid line is the true curve, the dots are the observed points. Let us take the group of seven points between the pair of dotted lines at the left. Assume that we are about to measure the central point of the group, just under the circle. We know that there are random fluctuations -- noise -- superimposed on the "true" value. We know, too, that the true curve must be a relatively smooth one in the interval over which we have taken the data. We can always be sure of this, if the points are taken sufficiently close together, and the ability to do this is one of the fundamental restrictions which must be placed onto any digital data recording system. Now a type of smoothing can be done in the computer which is hard to do in a spectrophotometer; we can "look ahead" of the point of interest as well as behind. Taking this group of seven points, we can proceed to fit a polynomial through them by least squares procedures, solve for y at the central point, and arrive at the "best" value of that point based on a least squares criterion.

Notice that we are not really interested in the coefficients of this polynomial (the "a's"), just in the value at the central point. With this restric-

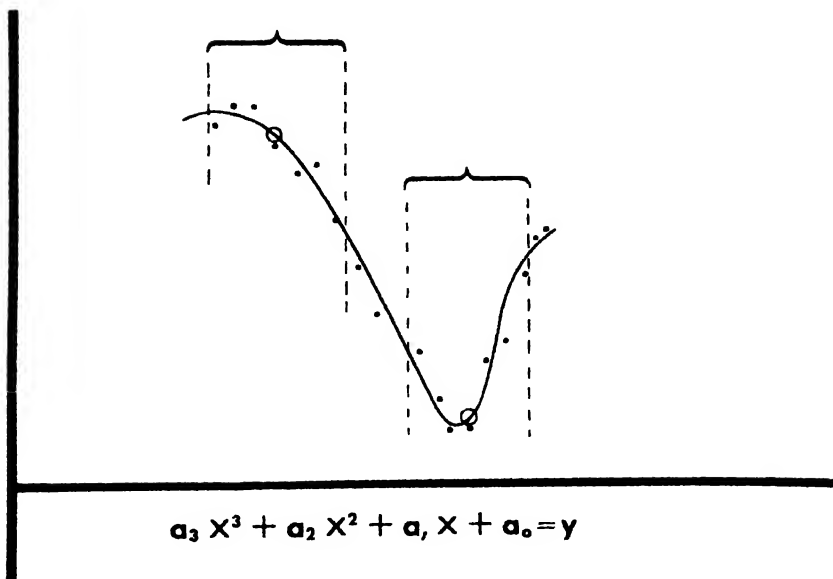


FIGURE 18-2. Representation of 7 point moving polynomial smooth (Reprinted from *Anal. Chem.* Vol 36, p. 1627, 1964. Copyright 1964 by the American Chemical Society and reprinted by permission of the copyright owner.)

CONVOLUTES — SMOOTHING — CUBIC (QUADRATIC)

Points	5	7	9	11
$x - 5$				36
$x - 4$			21	9
$x - 3$		2	14	44
$x - 2$	3	3	39	69
$x - 1$	12	6	54	84
x	17	7	59	89
$x + 1$	12	6	54	84
$x + 2$	3	3	39	69
$x + 3$		2	14	44
$x + 4$			21	9
$x + 5$				36
Normalize	35	21	231	429

FIGURE 18-3. Smoothing integers based on cubic (quadratic) least squares polynomial fit.

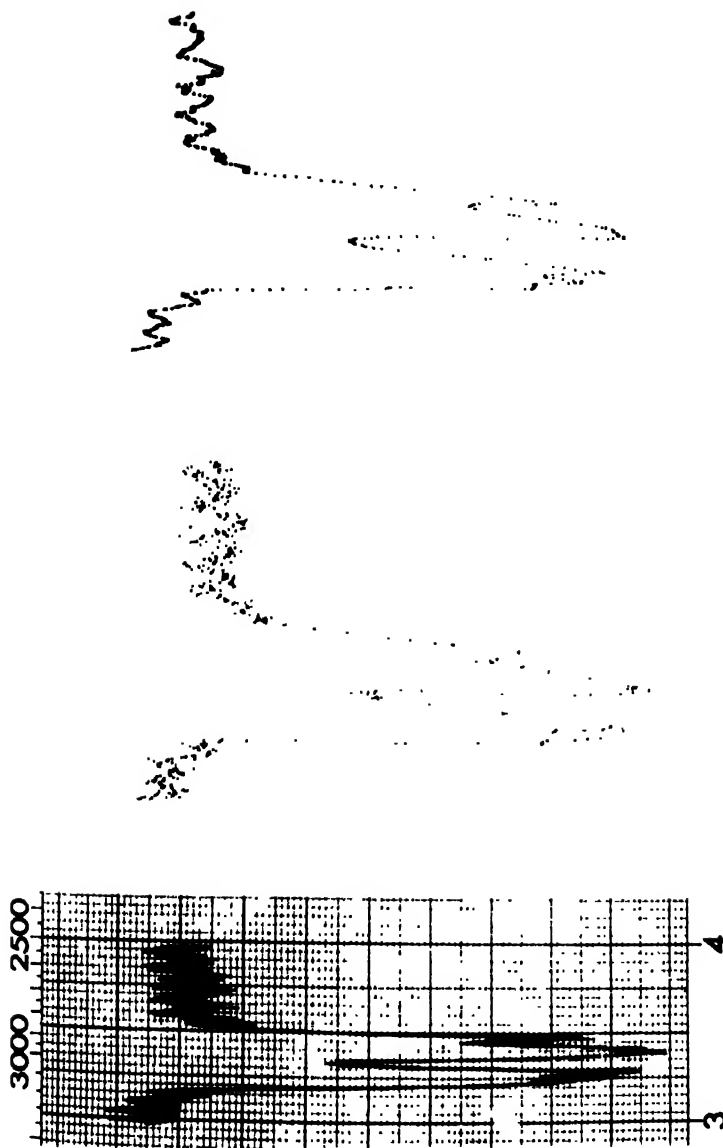


FIGURE 18-4. Example of 11 point smoothing of data collected under high noise conditions (sodium chloride prism):
 (a) Direct recorder tracing;
 (b) Raw data as recorded by the digital data recorder and plotted by the computer;
 (c) Plot produced by the computer following 11 point least squares smooth (integers in right hand column of FIGURE 18-3).

tion on the least squares procedure⁴² it develops that all one needs is a table such as the one in Figure 18-3 to find the best value at the central point of a set of numbers. For example, to obtain the best value for the center of the 7 points in Figure 18-2, one would use the column of the table marked 7, multiply the left-most point by -2 , and the next by 3, the next by 6, the central point by 7, the next by 6, and the next by 3, and the final one by -2 . These products are added and the sum divided by 21 to produce the answer. It is a very simple, rapid procedure. The process is called convolution of this set of numbers with our digital data.

Applying this process to the data, the result is the curve at the right in Figure 18-4. Here an 11-point convolute was used, taking the first 11 points, finding the best value of the 6th point, dropping the first point, adding the 12th, etc. The procedure is repeated for the 800 or so points shown, an impractical task for the human, but easy for the computer which never gets bored at such repetitive tasks. Notice the little shoulder at the left which was completely obscured in the original spectrum.

When filtering in a spectrophotometer, we almost always use a "time constant filter," shown schematically at the left in Figure 18-5. Note that this gives the greatest weight to the current reading, and exponentially less weight to older readings. The fall-off is quite slow, so that such filters have the characteristic of remembering a large noise pulse for a very long time. On the other hand, the least squares filter is completely symmetrical about the center point, and cuts off sharply 4 points away on *either* side of

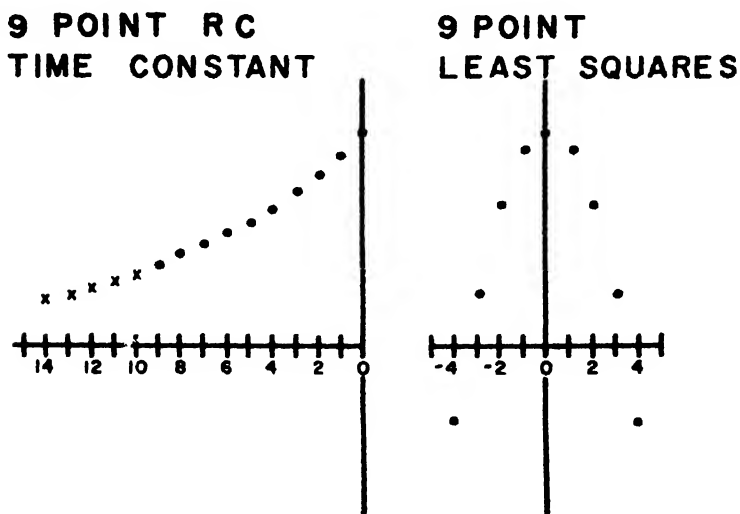


FIGURE 18-5. Digital representation of RC filter (asymmetric) versus least squares filter (symmetric).

the central point: it characteristically looks ahead as well as behind the point being examined, and therefore produces no dynamic distortion.

The least squares filters are like any other filter in their ability to reduce noise; that is, the use of 9 points reduces the noise by a factor somewhat less than 3, 17 points by somewhat less than 4—a square root relationship. In Figure 18-6 we have the raw data at upper left, 5-point smooth at upper right, and then 9-point and 17-point smoothing. For smoothing of long-term noise, it is necessary to make more than one run. The use of smoothing over a reasonable number of points, plus averaging of two or more runs, is a very powerful technique for noise reduction.

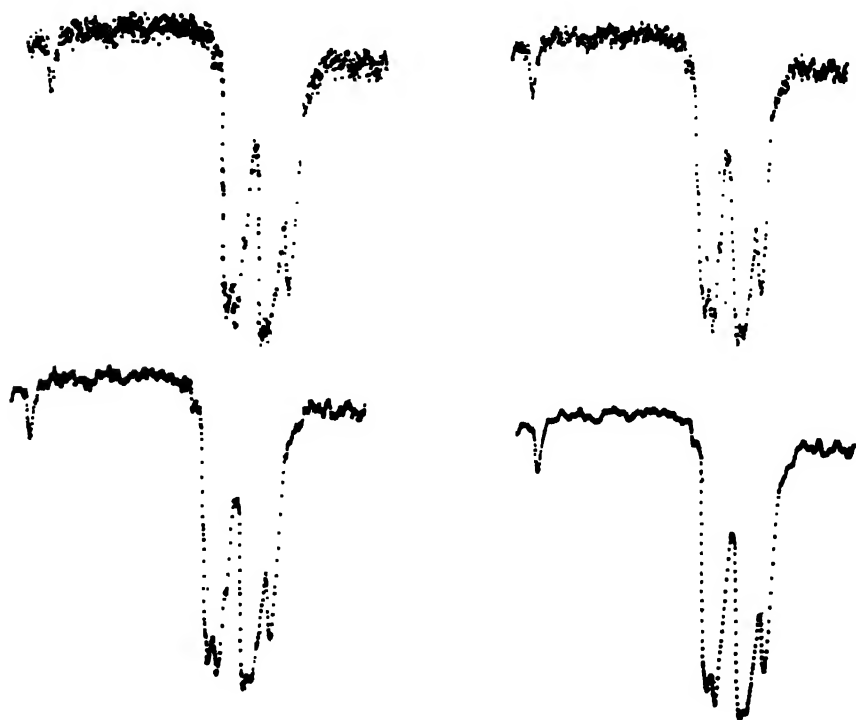


FIGURE 18-6. Effect of smoothing raw data using the 5-, 9-, and 17-point sets of integers. (Reprinted from *Anal. Chem.* p. 1627, 1964. Copyright 1964 by the American Chemical Society and reprinted by permission of the copyright owner.)

Smoothing Data and Determining Derivatives

One fact must be kept very clearly in mind. The usual time constant filter, in an instrument, is a piece of hardware—actual resistors, capacitors, servo system. But a computer filter is just a set of numbers entered into a

computer program. Both the shape of the "filter," as well as the program itself, can be changed practically instantaneously to suit any particular requirement.

Figure 18-7 is an example of a subroutine, written in the Fortran language, for performing the convolution of a set of data by a set of integers. This program is actually capable of doing much more than just smoothing of data. With different sets of convoluting integers, it can also be used to determine the derivatives---first, second, "nth" of a set of data. Figure 18-8 shows, at the right, the first derivative of the curve at left taken in

```

*      SUBROUTINE CONVOL                                A. AVILKY    JAN 1 1968
C
C      SUBROUTINE CONVOL(NMATA,NMATA1,NMATA2)
C
C      INPUTS VIA SUBROUTINE CALL
C      NMATA  NUMBER OF DATA POINTS
C      NMATA1 ARRAY OF DATA POINTS (0.01 INCHES)
C
C
C      INPUTS VIA CALLER AFTER SUBROUTINE CALL
C      (THIS IS A SUBROUTINE IN THE FORTRAN LANGUAGE)
C      NMATA1  NUMBER OF CONVOLUTING INTEGERS
C      NMATA2  NORMALIZING INTEGER
C      NMATA3  CONVOLUTING INTEGER = 5 FOR SMOOTHING
C
C
C      OUTPUTS
C      NMATA1  NUMBER OF CONVOLUTING INTEGERS
C      NMATA2  ARRAY OF CONVOLUTING INTEGERS (0.01 INCHES)
C      NMATA3  DATA IN MAIN PROGRAM
C
C      DIMENSION NMATA1(10), NMATA2(10)
C      DIMENSION NMATA3(100), NMATA4(100)
C
C      READ(10,10) NMATA1
C      NMATA1=1
C      NMATA2=NMATA1
C      DO 10 I=1,(NMATA1-1)
C        NMATA2(I)=NMATA1(I)
C      NMATA3(1)=NMATA1(1)
C
C      DO 200 I=NMATA1
C        DO 201 J=1,NMATA1
C          NMATA3(I)=NMATA1(I)+NMATA2(J)
C          NMATA4(I)=NMATA3(I)
C          NMATA5=0
C          DO 202 J=1,NMATA1
C            NMATA5=NMATA3(I)+NMATA2(J)+NMATA4(J)
C          NMATA4(I)=NMATA5/NMATA1
C        203 CONTINUE
C      2000 RETURN
C
C      101 FORMAT(5I8)
C
C      END

```

FIGURE 18-7. Convolution subroutine, written in the FORTRAN language.

this way. It must be emphasized that this differs from the usual analog method of determining the derivative in two ways. First, it is a derivative with respect to wave number and not with respect to time, and it is determined at each point *symmetrically* by looking ahead of the point of interest as well as behind.



FIGURE 18-8. (a) Transmittance spectrum—computer plot of digitized data (b) First derivative spectrum plotted by the computer following convolution of the transmittance data with point quadratic integrals). (Reprinted from *Anal. Chem.* Vol. 36, p. 1627, 1964. Copyright by the American Chemical Society and reprinted by permission of the copyright owner.)

Determining Band Positions and Intensities

Up to this point, we have seen a useful technique for the transformation of a large amount of data into another large amount of data. If this were all, while there would still be a case for the use of computers, it would not be a particularly strong one. Our purpose is to reduce materially, if we can, the amount of data with which we are to be confronted.

For example, we should certainly be able to get a table of band positions and intensities from the system. For this, we use the first derivative procedure to search along the spectrum, and we recognize the presence of a band by the fact that the first derivative changed from negative to positive.

This implies relatively smooth curves, of course, but this, in turn, depends upon the number of points used to determine the least squares first deriva-

tive. After finding the approximate location of the peak, the computer can draw a smooth curve through the data to determine the least squares absorbance and transmittance values at the peak. A 25-point first derivative, on an SDS 920 computer (which is 1/10 to 1/40 the speed of an IBM 7090), would take about a minute to perform this operation on a 10,000-point spectrum. The readin and readout of data would take longer than this. For reference, the spectrum from 2000 to 400 cm^{-1} contains 16,000 points when digitized at 1/10 wave number intervals. On our RPC 4000 computer the job would require 2 or 3 hr — if this seems a long time, remember that the table of band positions would represent readings of the spectrum to 1/10 wave number in abscissa, and 1/10% in transmittance, with scaling, correction for instrumental nonlinearity, etc. Obviously, such readability is not always needed, and if the data are obtained at 1/2 wave number intervals, all the times quoted are reduced by a factor of 5.

The Importance of High Density Spectral Recording

Fairly often, as I have discussed digitizing of spectra, I have been challenged on the requirement emphasized here, of high density recording of the spectrum. The point is made that if one examines the problem of gathering spectral data on the basis of Shannon's theory of information transmission, and let me emphasize that it *is* a theory of information transmission, only two samples per spectral slit width are needed to gather "all the information there is in the spectrum." While that may be true, Shannon made a basic assumption that is often overlooked in this context; he considered that he was transmitting bits — pulses whose shape he knew. But we don't know the shape of the spectrum line we are examining, and it is the shape of the spectrum line, and not the spectral slit width, that is determining. If the line is very broad relative to the spectral slit width, then only enough points are needed to outline the band adequately, assuming one knows there are no narrow shoulders that might be of interest. If the band is narrow relative to the spectral slit width, say 5 cm^{-1} with a spectral slit width of 1 cm^{-1} , then the theory seems to say that only 10 points are needed to outline the peak of the band. It is certainly enough if the shape of the band is known beforehand, and if there are no shoulders, and no noise.

The *proper* criterion is to take at least 2 points per *time constant*, since the time constant must be shorter, relatively, for narrow bands than for wide bands.

Spectral Line Shapes and the Finite Slit Width

One of the fundamental limitations in spectroscopy has always been that of finite resolution. While this is less of a problem with grating spectrophotometers, one is still often faced with very sharp, narrow bands, whose

shape and intensity are important. Jones^{19 20} has been investigating the shape factors of spectral lines, both intrinsically and as they are influenced by spectrophotometer characteristics.

There have also been studies of the finite slit width problem *per se*. If the spectrometer plot of an isolated spectral line is considered to be the result of a convolution of the actual line shape with the spectral slit width function of the spectrophotometer, the problem is essentially to deconvolute this function. A basic assumption of any of the deconvoluting procedures is that one knows the shape of the spectral slit width function of the particular instrument being used. This seems a tall order, and any approach to determine it will inevitably lead to some debate, but it can often be met by a bootstrap procedure using extremely narrow lines, lines significantly narrower than those to be deconvoluted. The use of Laser lines in this connection has been reported by Morgan.³³

Simple Deconvolution Procedure

A novel and quite simple approach to deconvoluting was published by Herget, Decus, Gordon, Lovell, and Nielsen.¹⁴ Figure 18-9 illustrates the resulting spectrum when a finite slit width has acted upon a narrow band. As is well known, the observed curve is broadened and reduced in intensity from the true curve. The deconvoluting procedure, which is based on an approximation method developed by Smith and Anderson of Oak Ridge, is illustrated in Figure 18-10.

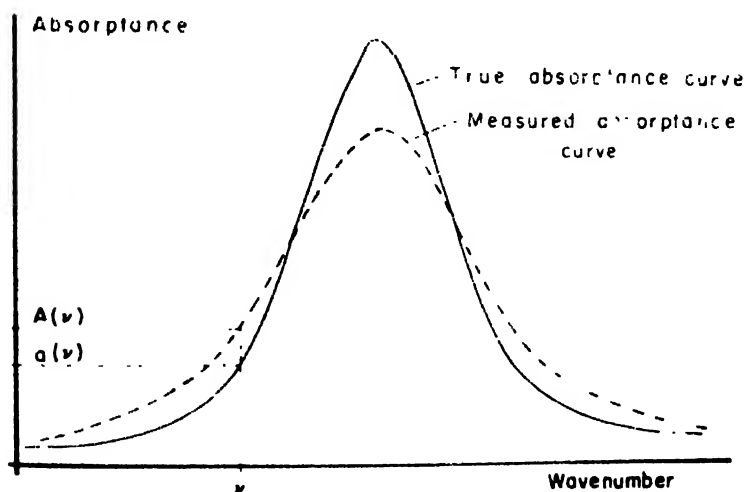


FIGURE 18-9. Typical true and measured absorbance curves showing the effect of finite slit width. (Courtesy of the Editor of the *J. Opt. Soc. Am.*)

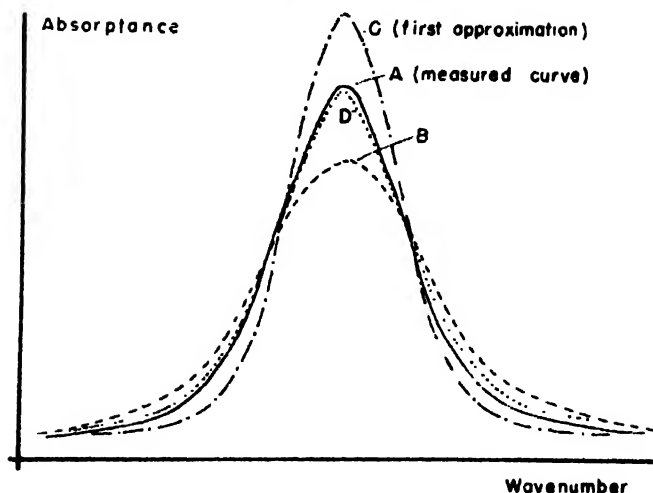


FIGURE 18-10. Procedure for correcting line shape for instrumental broadening. (Courtesy of the Editor of the *J. Opt. Soc. Am.*)

The observed curve, A, is first convoluted with the slit function. This results in curve B, which is still further broadened and reduced in peak intensity. The algebraic differences at each point between the observed curve, A, and the convoluted curve, B, are added algebraically to A to yield the first approximation, C, to the desired curve. C is then convoluted with the slit function to yield D, which is compared to A. If it matches, then C is the desired curve; if it does not match, the differences between A and D are added to C, and the process is repeated. It is stated that the third approximation was essentially identical with the measured curve, A, in all cases. It appears to be a fast, and potentially very useful, procedure. Subsequent work indicates that bands as narrow as twice the spectral slit width can be restored.

The Problem of Overlapping Bands

No matter how good these deconvoluting procedures are, and no matter how good spectrophotometers become in the matter of resolution, the problem of overlapping bands will always be present, since, in the most general case, the bands in a material will intrinsically overlap to some extent. One seldom finds materials where each band is completely separated from the next, but often it is necessary to examine the behavior of just one of the bands which appear in a group. Furthermore, if a spectrum could be resolved into its components, standard spectra would need to be only collections of the underlying band kernels — position, intensity,

half-width, and shape factor for each of the bands making up the spectrum, an enormous saving in data to be stored. Jones has shown, too, how even simple kernels can be built up to produce meaningful information in the case of steroid spectra.¹⁸

A number of groups have approached this problem, and only a few examples will be cited here. Biggers⁸ at Oak Ridge has been interested in the ultraviolet spectra of rare earths and their changes with temperature. Figure 18-11 shows the result of operating on a complex ultraviolet spectrum under the assumption that the underlying bands are Gaussian in shape. Some shape factor must be assumed in present programs, and it is generally either Gaussian or Lorentzian, and one may consider also the Voigt function which is a combination of the two. Stone⁴⁵ has published the results of a similar program which is capable of dealing with up to 10 bands; either Lorentz or Gauss, and a background term, for up to 900 points, and states that he will furnish a FORTRAN program deck to anyone requesting it. The program consumes most of the memory of a 7090, and takes about 5 min to converge on an adequate answer. That means about 100 hr on a millisecond computer, so it is not something to be undertaken lightly. As the techniques develop, this time will surely come down.

Both Stone's and Biggers' programs use a least squares matrix technique. Allen¹ has suggested correlation techniques as an alternate method of solution.

There are certainly many ways to approach the problem, and we can expect much work to be done in this area in the near future since it is of fundamental importance.

Quantitative Analysis

Advantages of Digital Readout Coupled with Computer Data Reduction. One of the most important and most obvious areas of application of digital recording and reduction of spectra is in quantitative analysis. Much of the earlier digital work was concerned primarily with quantitative analysis, for example, the work of Rogoff and Taplin of ITT, and Johnson and his group at Du Pont.

Among the many benefits to be derived is the one of reduction in the variability of the data due to operator judgements. Especially in those cases, where more than one operator is assigned to an important repetitive analysis, the use of digital readout coupled with computer data reduction means that precisely the same rules for reducing the data will be followed for every run. They are built into the computer program.

Furthermore, it is unnecessary, and indeed undesirable, to read precise base-line points and peaks. It has been repeatedly demonstrated that one should take a great many points—many more than the number of un-

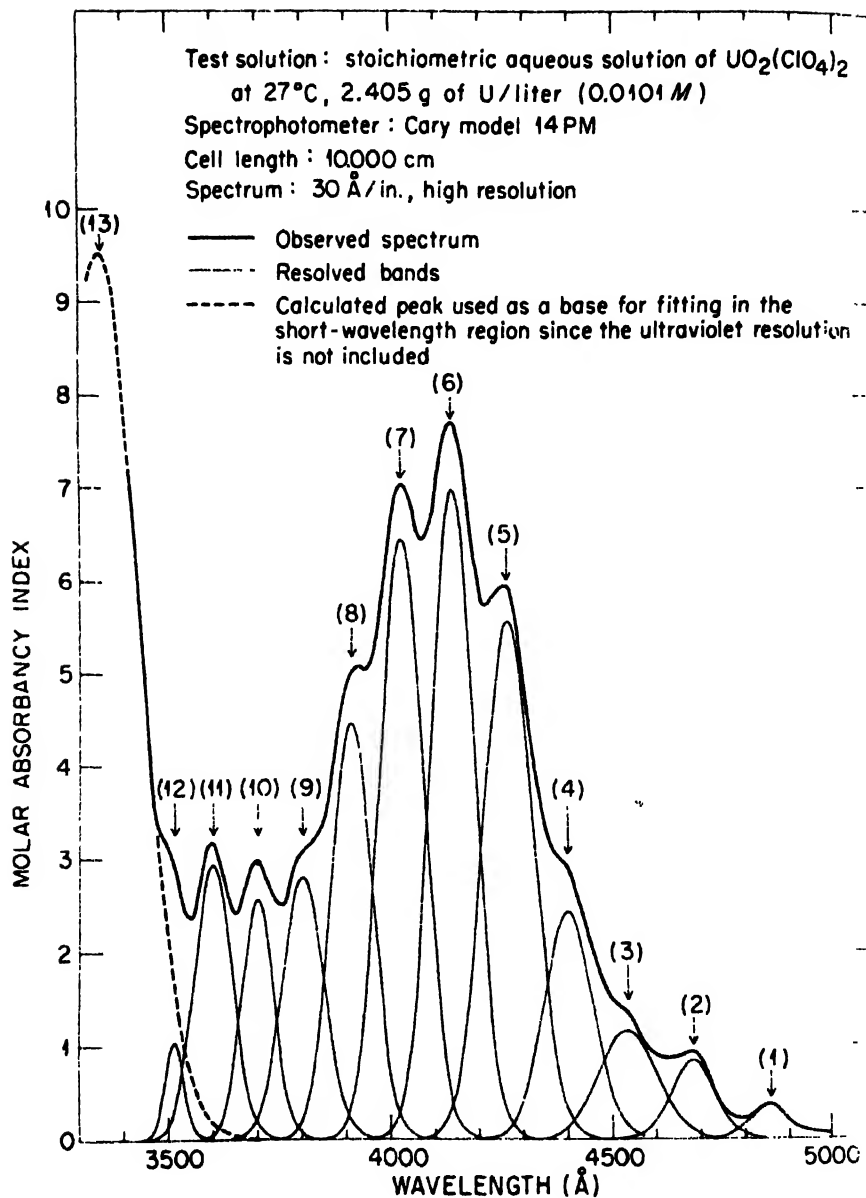


FIGURE 18-11. Computer resolution of overlapping spectral bands.
 (Courtesy of R. E. Biggers⁸)

knowns - in order to apply least squares matrix methods for consequent improvement in the results.⁷ Almost any computer installation is apt to have the necessary general purpose programs available in its program library. Sternberg *et al.*⁴⁴ have shown that for best results the data should be recorded at equal abscissa intervals, the same criterion required by the smoothing procedures, and the easiest requirement to implement in a digital recording system.

One can see, intuitively, how this improvement comes about. In the conventional multicomponent procedure, one takes as many readings as there are unknowns. Since the inaccuracies in reading are reflected in every component, the inaccuracies build up.

Obtaining many more points than there are unknowns means that the inaccuracies of reading are averaged over the large number of points taken. Furthermore, corrections required as a consequence of day-to-day variability in performance of the spectrophotometer, are quite readily applied.

Involved here, too, is the aspect of readability. In a properly designed digital system, every reading is made to $1/10$ of 1% in ordinate and $1/10$ wave number in abscissa, and this is independent of the scale on the recorder chart. Whether readability to these figures has real meaning is, of course, up to the other spectroscopic parameters.

Techniques for Mixtures. When the components of the mixture have very similar spectra, more sophisticated techniques may be applied. White *et al.*⁴⁶ described a linear programming method in which the computer itself selects those points which yield the greatest precision. Miles^{31, 32} uses the computer to form a synthetic spectrum built up from the spectra of the pure components of the mixture. This is then compared to the observed spectrum, corrections applied, and the procedure repeated until a satisfactory match is obtained. The errors in any matrix analysis can be studied¹⁶ by using a program which perturbs the input data, using random numbers according to the standard deviation of the measurement, to yield the standard deviation of the analysis.

One may desire to examine the spectrum of one of the components of a mixture free of the overlying spectrum of the other components. This is differential spectroscopy, of course; and if it can be done at all by the conventional double beam method, it should be done that way. But in certain cases it may not be feasible to prepare a cell of the pure background material each time; (it may be a degradation study in which the starting material no longer exists at the time of the second run), or it may not be possible or easy to adjust the reference concentration for complete cancellation. In this case, the computer can be used quite conveniently to "peel" the background from the spectrum. We know, of course, that there will be pertur-

bations in the spectrum due to the presence of the solvent, and therefore this technique is ideal for studying solvent-solute interaction.

Location of "True" I_0 . Another important use of digitized data is for the correction of background, or, more importantly, location of "true" I_0 . Crisler and Mencis* have applied the simple Beer-Lambert Law to data taken with a variable space cell. One spectrum is obtained with the cell at minimum thickness. A second spectrum is run at the minimum thickness plus nominal. The point by point ratio of these curves produces the "true" spectrum of the material free of instrumental background. The spectra of pure materials may be obtained at a series of thicknesses, the data corrected for finite instrument resolution, converted to absorbance, and stored on magnetic tape with a dynamic range unobtainable on a single instrument chart. Furthermore, from library spectra stored in this form on magnetic tape, a plotter can draw the spectrum at any desired concentration, and in any graphical format for comparison with an unknown.

Instrument Performance Improvement by Digital Methods. An important consequence of the fact that one has access to a general computer, and to a general purpose digital data recorder, is that the entire horizon of the laboratory is broadened. The smoothing techniques apply to any noisy measurement, such as NMR, fluorescence spectra, or rotatory dispersion measurements, and any necessary corrections can be applied to record the data in physically more meaningful units.

Basically, the use of digital methods (digitized data treated in the computer) provides a means of getting an improvement of some factor, 2 to 4 perhaps, in the information obtainable from that data. Therefore anyone working at the limits of performance of a particular instrumental technique should, without question, be thinking of digital methods if he requires performance improvement. This applies whether we are considering signal-to-noise problems, where smoothing or similar techniques would apply, or dealing with quantitative work, where we need photometric corrections, smoothing for dead band elimination, and many sampling points for improvement of the analytical matrix situation.

Digital methods provide the ability to correct for instrumental inaccuracies, compute absorbances, and, given adequate standards, to report molecular extinction coefficients.

Today, when a laboratory has gone to considerable effort to purify a sample in order to obtain a reference spectrum, it seems wasteful not to capture that same data in digital form; it's never too early to start building that all important library of digital spectra. Library spectra will be far easier to interchange on magnetic tapes than on charts, since there is no

*Private communication.

loss of accuracy in the reproduction of tapes and there need be no compromise on the scale or the quality of the printing, etc. While band kernels are the most efficient media of spectral storage, the start of a proper library should not be held up until kernelization methods are perfected. Once these methods are available, the digital library will need to be available to determine the kernels.

The Future of High Performance Instrumentation. It is interesting to speculate on the future course of high performance instrumentation. The field has come a long way in optical performance and readout capability. Much effort has been expended in the current generation of instruments in preserving all possible accuracy on the chart presentation. While chart presentation will never be discarded, it appears likely that the chart will be used just for monitoring the instrument performance, and the prime readout will be digital.

A laboratory with digitized instrumentation will, routinely, run check spectra at the beginning of the day. These will be examined by a computer program to determine that the instrument is running within specifications, and will be checked for day to day drifts in the manner of the familiar control charts. Any corrections necessary will be determined, and all runs for that day will receive abscissa and ordinate corrections and a minimum amount of smoothing before any further processing is attempted. These, then, take care of the day-to-day and instrument-to-instrument variations.

What will be done with the data thereafter is a function of the individual laboratory - the possibilities are as broad as the uses of infrared spectroscopy itself.

Section 2. Spectral Libraries and the Identification of a Spectrum

THE IDENTIFICATION OF A SPECTRUM

As stated in the prologue, this section has been deliberately separated from that on the use of computers in spectroscopy. The identification of a spectrum typically follows a hierarchy of procedures. The first is to "ask the man who might know." This is by far the most efficient, most rapid, and cheapest procedure. Failing here, one should turn to the non-mechanical procedures such as the Spec-Finder[®] or the Peek-a-boo (Ter-matrex[®]) or DMS Cards^{***} procedures, and finally to such mechanized

*Sadtler Research Laboratories, 3314-20 Spring Garden St., Philadelphia, Pennsylvania

**Jonker Business Machines, Inc., Gaithersburg, Maryland.

***The Documentation of Molecular Spectra, Butterworths Scientific Publications, 88 Kingsway, London, W. C. 2, England, and Verlag Chemie, GMBH, Weinheim, Bergstrasse, West Germany.

indexes as the ASTM IBM cards which can be searched by mechanical sorters or by computer.

The final operation in all these procedures, is the comparison of the unknown with a previously run, or published, spectrum. In this sense, all of the procedures provide *indexes* into the literature.

SPECTRAL INDEXES BY MACHINE METHODS

Machine methods (*not* computer methods) of forming spectral indexes are described by Baker, Wright, and Opler⁵ and by Kuentzel.²⁷ The Kuentzel system was adopted by the American Society for Testing and Materials (ASTM) Committee E-13,² and provides the foundation on which the Termatrix and all present computer methods are based.

The Kuentzel System

The basic element of the Kuentzel system is the IBM punched card illustrated in Figure 18-12. This card describes the "features" of the spectrum and of the molecule in terms of the *presence* of a band, or the *presence* of a functional molecular feature, by the *presence* of a hole punched in the appropriate position in the card. Thus, if the spectrum contains a band at 11.4μ , then a hole is punched in column 11, position 4, etc. The complete code is described in the book of codes and instructions available from ASTM.² The data in these cards come from published spectra. The last columns refer to the source of the spectrum. The actual coding is done by volunteer workers.

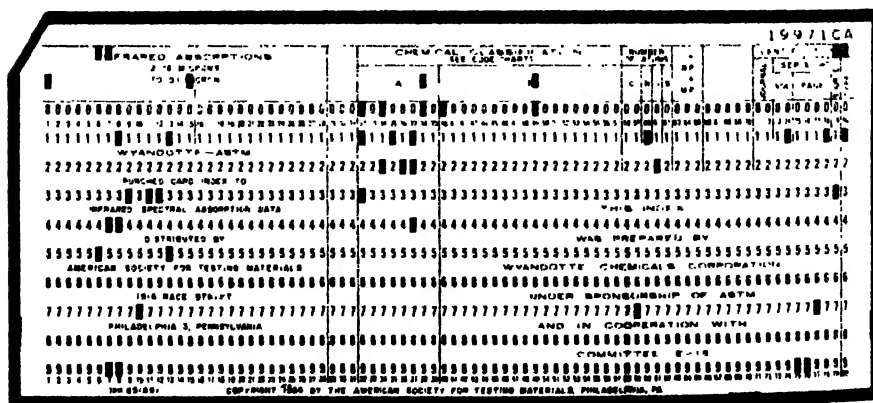


FIGURE 18-12. Punched card used in the Wyandotte-ASTM spectral indexing system. (ASTM, reproduced with the Society's permission.)

There were, as of 1964, over 64,000 cards from the various sources, which include all of the major collections of published spectra.

Searching the deck requires an IBM card sorter. A complete pass of the cards is made for each "feature" of the spectrum to be matched. This can be a long and tedious procedure, and therefore most users keep their cards in "pre-sorted" decks, one of which may contain all hydrocarbons, another all hetero-compounds, or oxygen only, etc.

The most powerful searches are those which look for all the cards in which a particular feature is absent. Thus if the material has *no* band at 3.5μ , sorting out all cards which show a band at 3.5 , and rejecting them, simplifies the search of the remaining cards. This *negative* searching is especially important if the sample is suspected of being a mixture.

SPECTRAL INDEXES BY NONMACHINE METHODS

The "Peek-A-Boo" System

By contrast with the basic IBM system, the "peek-a-boo" system exemplified by Termatrix is an inverted matrix system, or inverted index. Each new spectrum in the IBM system calls for a new card which contains all the data concerning that spectrum. In the peek-a-boo system there is a finite number of cards, each corresponding to a particular band interval in the spectrum. Up to ten thousand holes can be accommodated on a card. These hole locations correspond to *serial numbers* of the coded spectra. Thus, the card for 8.5μ would contain holes corresponding to the serial numbers of all those compounds which exhibit a band at 8.5μ . Similar cards are generated for each of the spectral features to be coded.

A search consists of selecting the cards corresponding to the features to be identified, stacking the cards on a light-box, and looking for the spots of light (hence peek-a-boo!) which identify those spectra which contain all of the features in common.

As a nonmachine method, it is simple to use in the laboratory. It is especially adaptable to "browsing," where one selects a particular group of features, stacks the appropriate cards, and then asks "how many more answers do I get if I don't require the presence of a 10.2μ band?" or "how is the field narrowed if I require the absence of a band at 7.6μ ?"

The basic information for producing the Termatrix cards is obtained from the ASTM card index.

COMPUTER TECHNIQUES FOR SEARCHING THE IBM CARD FILE

At the other end of the accessibility spectrum lie the various computer techniques for searching the IBM card file. This, too, was accomplished

under a special task force of committee E-13. The earliest program was produced under Lee Smithson at Wright Patterson Air Force Base for the IBM 7090 computer.⁴³ Their technique has subsequently been adapted to other computers.

The information on the complete file of ASTM cards is written onto a single reel of magnetic tape. A search request consists of a sequence of logical requests such as "Band at 7.4. or 7.5 and 8.6 or 8.7 or 8.8 and not 11.6 or 11.7 . . . This request is coded onto punched cards, and entered into the computer.

The computer then compares each item in the magnetic tape file against the request and arranges the answers in descending order of match frequency. Up to 10 matches are retained for each request, and up to 36 requests may be examined in a single 18 min computer run. The searching speed is limited primarily by the speed at which the library information can be read from the magnetic tape.

On other computers, the number of requests and speed of processing are often limited by computer memory size or slow internal speed. The most efficient searches are conducted on those computers which have a "binary word" capability, such as the IBM 7090, although programs have been produced for "business oriented" computers as well.

ASTM committee E-13 has acted as the spark and collection point for the various computer programs available, and ASTM should be consulted to determine availability of programs for particular computers.

A basic limitation of the current computer procedures is the difficulty of "browsing" except by specifying alternative searches. In the future, however, we can expect remote consoles to be developed for the large computers, and the information placed on magnetic disc memories for more rapid access than magnetic tapes. Then one can develop quite efficient procedures based on the inverted matrix technique in exact analogy to the peek-a-boo system, but capable of handling the complete ASTM index at once.

CONCLUSION

The search for a match to an unknown spectrum may often lead far afield. The complexity and extent of the search will always be a function of the importance and of the difficulty of finding the match. At present the index entries consist solely of band position, indication of the strongest band in the spectrum, and the molecular information. Although limited, it is a large amount of information and often yields adequate results. It would appear desirable to add some intensity information, but this will require new coding schemes, and new techniques of searching. In the mean-

time, this retrieval problem should never be confused with the use of computers for the extension of the spectroscopic information.

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